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Principles of su

PRINCIPLES OF SUGAR TECHNOLOGY

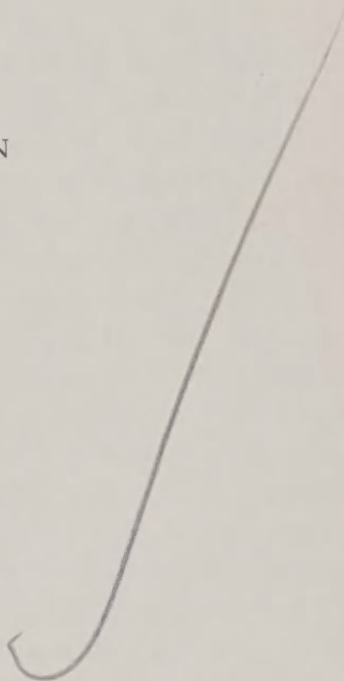
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VOLUME II
CRYSTALLIZATION

TMB



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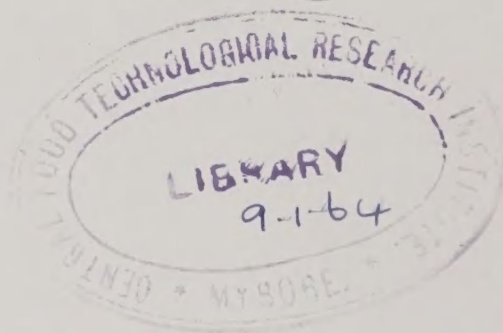
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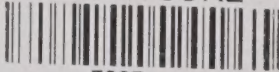
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PREFACE

The presentation of the experience of a number of sugar technologists working in different countries and with varying backgrounds is like a Round Table discussion where each of the contributors presents his ideas on one general subject. It is unavoidable that the way the experience of one writer is described is occasionally slightly different from what others say on the same subject. This is the result of discussions where each of the participants is giving his contribution to a general idea and where it is found that although the purpose is identical, the manner in which observed facts and theories are presented in the form of general ideas and recommended operational techniques shows some variation.

The editor asks the reader to keep in mind that the main object of this book is to give a complete summary of the principles of the crystallization process as it is applied today in the sugar industry over the whole world, with a description of the control systems and theories concerned with crystallization.

Our endeavor is to present our knowledge on this subject as it is today. The immediate motive is in the first place to supply our colleagues with a review on this rather complicated technological process in sugar manufacture. The editor acted as a kind of a master of ceremonies who asked for and received the courteous cooperation of his colleagues whom he has known for many years by their original studies in this field and whom he feels have made valuable contributions to progress in the practical technology as well as in the theory of crystallization.

The various papers must under no condition be seen as a final codification of the science of sugar crystallization. In the field of crystallization we are only able to state the present way of thinking and operating; but every technologist knows that there are still many unsolved questions which can only be answered properly by careful experimentation and observation, which will require the whole energy and devotion of many experimenters who are attracted to this field of study.

We expect that this presentation, a diffusion of available experience, will also assist in clarifying some of the vague ideas on crystallization written down in words, thereby acting as a catalyst for further verification and study.

This book is not a collection of papers which can be reviewed and read in a few hours; it requires careful reading. The more critical the reader is about the statements made by the contributors, the greater we feel the value

of this book will be for continued progress in sugar technology. This book is also educational if we accept the fact that the experienced technologist, after he has left the institute for professional training, requires a confrontation with what others have experienced in the same field in order to find out the hiatuses in his theoretical knowledge.

Although the editor of this book is a pupil of the scientific school of thought that the terminology and expressions we use must be as exact as possible, he is at the same time aware of the fact that a number of terms that have been introduced in the crystallization process, as, for instance, the quantitative expression for supersaturation, still pose a problem. A tremendous amount of study in the field of pure physics and chemistry will have to be done before we have a complete understanding of the nature of supersaturated sugar solutions.

The quasi exactness introduced by formulae to calculate the degree of supersaturation does not tell us the whole story about the nature of the sucrose in supersaturation, about the significance of supersaturation for nucleation and the exact nature of crystal growth. The formulae and equations we are applying today are a crude approximation to classify the observed facts, but we are not able by these formulae to express the exact nature of the phenomena taking place in crystallization.

The progress that has been made in crystallization from a practical point of view is that we are able to control the crystallization process by methods far superior to the traditional control systems as used by experienced pan boilers. A complete analysis of the crystallization characteristics of different types of sugar solutions is still a goal far removed from our present knowledge.

It is, in the practical sugar industry, a deplorable situation that the art of practical sugar making and fundamental investigations of the different processes we are confronted with in operating factories are so far away from each other. A number of fundamental studies on the principles of sugar crystallization must be done in institutes devoted to research and scientific investigations. The results of these studies must be translated into the language of operating technologists and into applicable rules for the practical crystallization process.

We have avoided in the presentation of the different phases of the crystallization process complicated theories on crystallization phenomena, however attractive this may be and despite the fact that we are convinced that a number of these more theoretical studies might be of practical value to the industry. We have kept in mind that this book is primarily for the sugar technologist connected with modern factories who has solid knowledge of the

principles of chemistry, physics and chemical engineering. Every contribution is written in simple and understandable language. Mathematical theories have been left out, because in this developmental phase of the crystallization process they are not yet of practical meaning to the sugar technologist in charge of a refinery or sugar factory.

We feel that this book has been written and composed so that it can be read at leisure by everyone connected with the sugar industry, and be used as a reference book to refresh the reader's knowledge and enable him to compare his experiences or ideas with what his colleagues in different countries have been studying and what they have written regarding their ideas.

We hope that when using this book, the reader will insert question marks and marginal notations, and when he can find the time will let the editor know what he agrees or disagrees with and will supply him with any additional information he may have on this fascinating subject of sucrose crystallization.

We are presenting also the views of our able colleagues on the crystallography of sucrose, which is a very neglected field in the training of sugar technologists, on the procedure of crystallization technique, on control methods, and on fundamental changes and evolutions in the equipment used in factories for the crystallization process.

It is to a certain extent surprising when one has the opportunity to read the professional literature of the past century, to observe that it was in 1885 that L. WULFF got his first patent for crystallization in movement (DRP 33.190, *Z. des Vereins* 35 (1885) 899), which was the beginning of the introduction of crystallizers in the sugar industry. This beginning is practically no more than a lifetime from today.

The developments in the technology as to crystallization by cooling, our increased knowledge of the solubility of sucrose in impure solutions, the introduction of control instruments and the technological and engineering developments in vacuum control and adjustment, the regulation of vapor pressures, a better understanding of the significance of the circulation in vacuum pans, the nucleation technique; these are all results of the work that has been done in the past 70 years.

That the methods in different areas of sugar production still show considerable differences is partly caused by the fact that the exchange of information is not perfect. Local tradition and nationalistic chauvinism are also involved in many techniques, however strange it may seem that in this field of applied science there should still be room for sentimental feelings. But it is nevertheless a psychological element in the spread of new ideas,

which can be observed by careful analysis of working methods as locally applied in the different sugar-producing countries.

We have tried to present this book by giving the views of technologists living in different countries, thereby ensuring the most complete presentation possible. It is not only a matter of local tradition how problems are discussed and presented, but it is a part of the education of each of us.

The specific problems receiving our interest are to a great extent the result of our education and the way our teachers have been able to arouse our interest in certain subjects. Later on, it is the facilities available to us in the daily duties we have to perform which direct more or less the kind of investigations we have the good fortune to make. The world is progressing to a more liberal and also more intense exchange of experience and knowledge. By asking the cooperation of his colleagues, the editor intended to present this whole field from an international point of view, avoiding as much as possible the local or personal approaches to the crystallization of sugar.

I feel extremely privileged that my colleagues for whose cooperation I asked have given support in such a generous way. I wish to express my sincere gratitude for this assistance in the realization of what I have always seen as one of the main aims of my professional career, the sharing of experience with my colleagues, and in this way the creation of an atmosphere of cooperation, which is the most effective way for progress.

Grateful acknowledgement is made to Mr. EDWIN I. KILBOURNE, President of the West Indies Sugar Corporation who has given me the opportunity to work on this book during my activities for that company.

A word of special gratitude is expressed to my secretary, Miss GERDA VAN WAASBERGEN, for her help in preparing the manuscripts and for everything connected with the editing of this book.

P. HONIG

New York, N.Y., December, 1958

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CHAPTER 1

CRYSTALLOGRAPHY OF SUCROSE

H. E. C. POWERS*

Chief Chemist, Tate & Lyle, Ltd., Thames Refinery, London (England)

1. Introduction

According to the Oxford English Dictionary the word 'crystal' has been derived from the Greek word *krystallos*, meaning clear ice or rock crystal. Its original meaning implies the usage of the word as a descriptive adjective, e.g. 'crystal clear' or 'crystal like'. The precise and scientific application of the word 'crystal' is: 'a form in which the molecules of many simple elements and their natural compounds regularly aggregate by the operation of molecular affinity. It has a definite internal structure, with the external form of a solid enclosed by a number of symmetrically arranged plane faces, and varying in simplicity from a cube to much more complex geometrical bodies'.

For the sugar refiner the word 'crystal' is therein used as follows: 'Crystals: a particular quality of refined crystallised sugar', or 'There are three classes of sugar refineries in this country, the chief productions of which are, respectively, (1) loaf sugar, (2) crystals (*i.e.* large, well formed dry white crystals of sugar), (3) crushed sugar'.

Having touched upon the etymological history of the word crystal, it is natural to consider when sucrose crystals first became known, as such, to mankind. E. O. VON LIPPMANN** has given us probably the most authoritative and inclusive history of sucrose in his *Geschichte des Zuckers*. From this source it is apparent that the similarity of the word for sugar in many languages stems from the initial Sanskrit word *Sarkara*. The Persians appear to have been among the earliest to develop specific refining technique and to produce, at will, crystals as we know them. About 500 A.D. in Persia

* DR. A. F. SEAGER of Birkbeck College, University of London, has prepared sections 3 and 4, also the crystal drawings and projections, utilizing the earlier report of F. P. PHELPS⁵ and the specimens of sucrose crystals made available by H. E. C. POWERS.

** E. O. VON LIPPMANN, *Geschichte des Zuckers*, 2nd Ed., J. Springer Verlag, Berlin, 1929.

the term *kandi-sefid* is on record as meaning white sugar, implying some ability to obtain a purified form by crystallisation. The still older Indian term *shekar* or *shakey*, an early form of the word sugar, probably referred to evaporated juice now known as *gur*. We may deduce that 'crystals' became the special study of some keen folk in the early centuries A.D., since they had to depend for the separation of crystals and mother liquor upon simple drainage under gravity. This would have presented a real incentive to produce large crystals. One may deduce that the technique of growing of *kandi* crystals is a development of the early need to grow large crystals.

Revolutionary advances in commercial sugar production were made possible first by the development of the vacuum pan in the early years of the nineteenth century, and next by the centrifugal machine about 1837. The first permitted the operator to grow fairly regular crystals rapidly and without serious decomposition hence colour formation. There would still have been a considerable incentive to grow well formed uniform crystals, in order either to improve the separation of the syrup under normal gravity, or under the early low power centrifugal drainage. This urge should still be with us, even though the introduction and the development of the powerful modern centrifugal machine has made too many of us somewhat callous of the ultimate improvements possible with really good grain production.

It is worthy of thought that sucrose shares with salt a somewhat unique position, in that not only are they both regarded as among our most important foodstuffs, but they are also both chemicals capable of the utmost purification by methods normal in the chemical industry. Few analytical chemicals can be purchased at the astonishingly high degree of purity achieved in the production of millions of tons of refined sugar annually. It would be fair to claim that this would not have been possible without the efforts of many generations of workers who, whether they realised it or not, were practical students of crystallography!

With this introduction, we need make no apology for attempting to outline some of the more scientific principles involved in crystallography. If my efforts produce an arrangement in a form attractive to the readers and my colleagues in the sugar industry, then I shall be content.

The natural laws of crystallography apply to substances so diverse as non-polar organic chemicals like sucrose, ionised soluble salts like sodium chloride, practically insoluble substances such as silver bromide, and to metals crystallising from the molten state. Differences in analogous phenomena at first tend to cause confusion, but usually disappear as the gaps in our knowledge are filled in. In our industry we can benefit by co-operation with the scientists working in other industries, and of colleagues with

insufficient time or opportunities to study any unusual, interesting or challenging observations we ask them to put them forward, as the cumulative effort and interest would be most helpful.

2. Characterization of a Crystal

Whilst one can name a number of substances which we call crystalline, yet there are a large number of materials which could only be classified as crystalline by an expert. Even refined sugar can be made in such a form that it is not evident to the uncritical observer to call it crystalline or the same crystalline material we are familiar with. Those familiar with the literature will remember the remarkable collections of strikingly different sugar crystal forms published by workers as WOLF¹, WULFF², GROTH³, PHELPS⁵, SANDERA⁶, VAVRINECZ^{7, 8, 9, 16} HONIG¹⁸ and many others. Sucrose occurs in a number of solid forms, which have not received general attention. We may have pulverised forms, fondant sugars, spray-dried sugars – each and all have the virtually identical analysis of highly refined sugar, yet present different physical properties.

The cumulative studies of a number of workers in different fields have enabled us to order our thinking. In the following pages we have related something of the present state of our knowledge of solid sucrose.

The essential feature of crystalline matter is that the molecular structure shall be orderly, in a specific pattern characteristic of that particular material. How is the scientist to determine whether a particular substance exhibits this orderly molecular structure? X-ray analysis provides delicate and wonderful means to achieve this (BEEVERS and COCHRAN¹¹).

Spray-dried sucrose is non-crystalline. PALMER¹⁹, and MAKOWER and DYE²⁰ have demonstrated the extremely high hygroscopicity of this substance, and that it may take months or even years to crystallise when stored under conditions of low humidity. Under the microscope the particles appear as minute spheres, and though it is often spoken of as amorphous sugar, it can also be considered as a supercooled fluid.

All the other forms of sucrose, as *e.g.* listed above, are truly crystalline. This can be demonstrated by X-ray analysis, even though they may to the eye and touch appear as impalpable powders.

3. History of and Introduction to Crystallography

DR. A. F. SEAGER

Before dealing with the crystallography of sucrose itself it may be of interest to give a very brief history of that part of the science of crystallography which deals with the shape of crystals (morphology) and their symmetry.

(a) *The Morphology of Crystals*

It is quite understandable that the characteristic of naturally occurring crystals first to attract the eye of man should be the development of plane faces or facets at regular angles, and the brilliant reflecting surface which many of these faces present. The first recorded observation of this kind seems to have been made by PLINY THE ELDER about A.D. 77 in his *Natural History*, in which he comments on the regular hexagonal form of quartz crystals and the high natural polish to be seen on their faces.

The Greek word *krystallos*, meaning ice, was used in the Middle Ages for rock crystal, a clear variety of quartz. ALBERTUS MAGNUS used the word in this sense in 1250, under the impression it was ice frozen hard by the low temperatures prevailing on the mountains in the Alps. The word crystal now has a much wider meaning, being applied to all substances, whether naturally faceted or not, which have a regular internal atomic structure.

NICOLAUS STENO, in 1669, was the first to announce the law of the constancy of interfacial angles on crystals, as a result of approximate measurements on rock crystal. He was a man of wide interests, his official position was that of Professor of Anatomy in the University of Copenhagen but he was also a geologist. Steno's deductions from quartz were confirmed as a general law of nature by GUGLIELMINI, who published two memoirs on the subject in 1688 and 1705.

CARANGEOT, Romé de l'Isle's assistant, invented the contact goniometer in 1780. This was a semicircular protractor, graduated in degrees, with an arm pivoted at the centre of the scale. By placing two faces of a crystal along the edge of the protractor and the arm, the angle between those faces could be read on the scale. By means of numerous measurements with the contact goniometer Romé de l'Isle was able, in 1783, to verify the law of the constancy of interfacial angles with greater accuracy than had been possible hitherto.

The greatest advances in the early development of crystallography were made by the Abbé RENÉ JUST HAÜY, who has often been called the Father of Crystallography. He was at one time Professor of Mineralogy in the Museum of Natural History in Paris, and also an honorary Canon of Notre Dame. HAÜY's work spanned the fields of crystal morphology and structure and provided a great stimulus for future work. In 1784 HAÜY published an essay on a theory of crystal structure, based on a study of the cleavage or plane fracture of crystals. With the aid of this theory he was able to demonstrate that all the numerous faces which may appear on crystals are related

in a simple way to the crystal structure and to each other. He showed that if a suitable set of axes, usually three, is chosen within the crystal, these may be used as co-ordinates to define the orientation of all the faces. The ratios of the lengths of the intercepts which a face (produced if necessary) makes on the axes was shown to be simply related to the ratios of the intercepts of other faces. When suitable units are chosen, the ratios of the intercepts of a face are all found to be small, rational whole numbers. This relationship is often called the Law of Rational Indices, the reason for which will be apparent after indices have been described. Crystals were thus seen to possess a high degree of order. HAÜY also announced that every crystalline substance possessed its own crystalline form. These were great and important advances in the young science of crystallography.

(b) *The Symmetry of Crystals*

In the period from 1830 to 1867 much attention was paid to the symmetry of the external form of crystals, work which is associated with the names of HESSEL, GADOLIN and VON LANG. Crystals may exhibit symmetry of three kinds: about a plane, about a line and about a point, known respectively as a plane of symmetry, an axis of symmetry and a centre of symmetry. When a plane of symmetry passes through the centre of a geometrically perfect crystal it divides the crystal into two parts, equal in size and shape, which are mirror images of each other. When a crystal is rotated through 360° about an axis of symmetry it presents the same aspect to the observer on two, three, four or six occasions, depending upon the degree of symmetry shown by the axis. When a crystal possesses a centre of symmetry, a line passing through any particular point on its surface, when produced an equal distance on the opposite side of the crystal will pass through an identical point. The crystallographers mentioned above were concerned to find the number of different types of symmetry possible in crystals. They all agreed eventually that only 32 types of symmetry were possible in the external forms shown by crystals. Each of these types was called a 'class' of symmetry. It is interesting to note that at the time their work was carried out only a few of the possible 32 classes had been observed. The 32 classes of symmetry are grouped into seven 'systems', which each have certain characteristics in common, namely the crystallographic axes. These are the axes, mentioned above, used to define the orientation of the faces on a crystal. In the cubic system there are three crystallographic axes of equal length at rightangles to each other. In the tetragonal system there are three crystallographic axes at rightangles, two of which are of equal length, while

the third is longer or shorter. In the orthorhombic system there are three crystallographic axes at rightangles of unequal length. The monoclinic system is defined by three unequal axes, two of which are at rightangles, while the third is inclined. In the triclinic system there are three unequal axes, none of which are at rightangles. The hexagonal system has three equal axes at angles of 120° , with a fourth axis at rightangles to them which may be longer or shorter. In the trigonal system the same axes as in the hexagonal system are sometimes used, or otherwise three equal inclined axes, parallel to the edges of a rhombohedron.

(c) *Indexing of Crystal Faces*

It is most desirable to have some precise method for referring to each of the faces which may be developed on a crystal. The method which is almost universally adopted nowadays is called the Millerian system of notation, named after Professor W. H. MILLER of Cambridge. In 1839 MILLER gave this notation widespread publicity by using it in his *Treatise on Crystallography*, although the method had been suggested earlier by the Rev. Dr. WHEWELL.

In general a set of three axes within the crystal is chosen as co-ordinates. These are known as the crystallographic axes, and have the characteristics mentioned above for each of the crystal systems. The axes usually chosen are parallel to the edges of the parallelepiped of the unit cell of the crystal, and this parallelepiped may be considered to enclose one unit of the structure of the crystal. The directions of the crystallographic axes are therefore not arbitrary, but correspond to important directions in the crystal lattice.

In the orthorhombic system, for example, there are three crystallographic axes at rightangles, all of different lengths, so that the unit cell has the shape of a common brick. A conventional orientation of the axes has been adopted, the reading position, so that crystals may be described in a uniform manner. In orthorhombic crystals two of the crystallographic axes are placed horizontal, one running from front to back and the other from left to right, while the third axis is necessarily vertical. For brevity letters are assigned to the axes, the front-to-back axis is designated *a*, the left-to-right axis is called *b*, and the vertical axis is *c* (Fig. 1/1).*

Let us consider an orthorhombic crystal with the shape of a brick, in which the lengths of the sides parallel to the

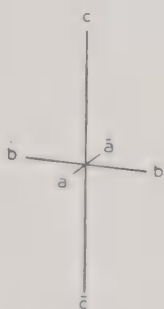


Fig. 1/1

* Figs. 1/1-1/29, the drawings and projections of crystals, are executed by DR. SEAGER.

a -, b - and c -axes measure $\frac{1}{2}$, 1 and 2 inches respectively (Fig. 1/2). For simplicity it will be imagined that the ratios of these lengths also represent the ratios of the lengths of the three sides of the unit cell, so that the axial ratios (the ratios of the lengths of the crystallographic axes) will be $0.5 : 1 : 2$. Now consider the front face of the crystal. This will cut the a -axis but will be parallel to the b - and c -axes. Since this face only cuts one axis we can, for simplicity, call the intercept made on the a -axis by the front face one unit of length. The Miller symbol of a face is obtained by first writing successively the intercepts made by that face on the a -, b - and c -axes respectively, using the correct units of length for each axis. When a face is parallel to an axis the intercept may be written as infinity. The intercepts made by the front face of the crystal on the three axes will be one, infinity and infinity. The actual Miller symbol consists of three indices which are the reciprocals of the intercepts, in this case (100), as shown in Fig. 1/2. It is customary to place the symbol of a face in round brackets, as shown. This symbol is read as three separate indices, 'one, nought, nought', and not as 'one hundred'. The back face of the crystal will clearly have a similar symbol, for it will cut the a -axis at the back and be parallel to the b - and c -axes. To distinguish between these two faces the back end of the a -axis is regarded as negative, and a minus sign is placed over the first index to represent a negative intercept on the a -axis ($\bar{1}00$), which is read as 'minus one, nought, nought'. The vertical face at the right-hand end of the crystal will have the symbol (010), and its opposite parallel face will be (0 $\bar{1}$ 0), since the left-hand end of the b -axis is taken to be negative. The c -axis is regarded as positive at the top and negative at the lower end, so that the upper and lower horizontal faces of the crystal will have the symbols (001) and (00 $\bar{1}$) respectively. The faces on crystals will usually be found to fall into groups of two, three, four or more having similar characteristics, such as lustre and surface markings, which have the same size and shape when the crystal is perfectly developed. Such a group of faces, all related to each other by the symmetry of the crystal, is called a 'form'. On the crystal discussed above the six faces fall into three pairs of parallel faces, those in each pair having the same size and shape. Each of these pairs constitutes one form. A form is indicated by taking one face in which all the indices are positive, if possible, and placing its symbol in braces, thus {100}. The form {100} comprises the two faces (100) and ($\bar{1}00$).

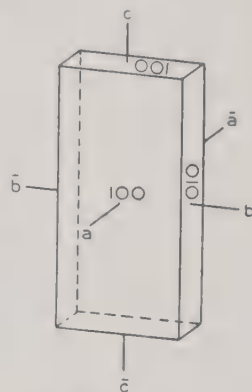


Fig. 1/2.

It is convenient to consider the crystal as built up of small structural units which have the shape of the unit cell. In the case of orthorhombic crystals this unit is of the shape of a brick, but the dimensions will vary from one substance to another. A larger composite body, with the same relative proportions as the structural unit, can be made by stacking the smaller units together in the appropriate manner. Fig. 1/3 shows such a crystal composed of seven lattice units in width, depth and height. This is the simplest method of stacking such units.

When the structural units are stacked in other ways new forms are developed on the crystal. Fig. 1/4 shows the same general structure as in Fig. 1/3, but with structural units omitted systematically from the vertical edges,



Fig. 1/3.

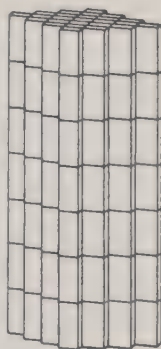


Fig. 1/4.

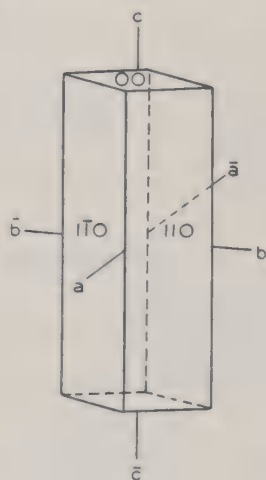


Fig. 1/5.

parallel to the c -axis. When a path is traced from the front of the crystal to the right-hand side, it will be seen that for each unit step to the right there is a unit step to the back. In other words, for each unit step along the b -axis there is also one along the a -axis. Since the structural units are exceedingly small and quite invisible the crystal actually appears as in Fig. 1/5, in which each vertical face cuts the a - and b -axes at one unit of length, and is parallel to the c -axis. The symbol of the front right-hand face is (110) . A form with three or more faces parallel to the c -axis is called a prism. This prism, $\{110\}$, has four faces, the symbols of the other three being $(1\bar{1}0)$ front left; $(\bar{1}\bar{1}0)$ back left; and $(\bar{1}10)$ back right.

Fig. 1/6 illustrates another modification of Fig. 1/3 in which the lateral edges parallel to the a -axis have been truncated, or replaced by a face. The normal appearance of the crystal is shown in Fig. 1/7. This truncation gives another four-faced form, in which each of the faces cuts the b - and c -axes and is parallel to the a -axis. The symbol of this form is $\{011\}$, and

comprises the faces (011) , $(01\bar{1})$, $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$. Such a form is often called a dome.

Fig. 1/8 and 1/9 illustrate another form obtained by truncating the edges of Fig. 1/3 which are parallel to the b -axis. The symbol of the form is $\{101\}$,

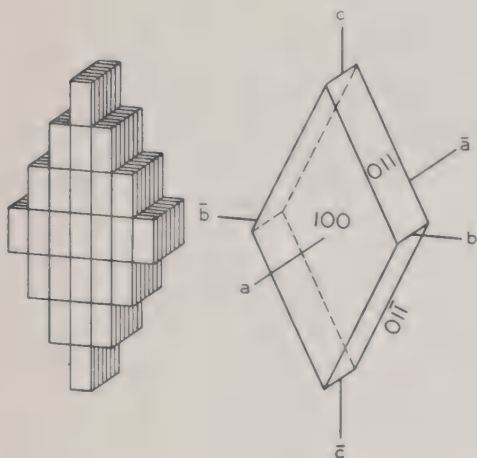


Fig. 1/6.

Fig. 1/7.

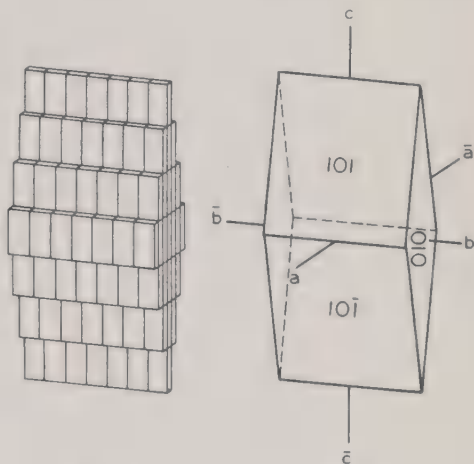


Fig. 1/8.

Fig. 1/9.

comprising the four faces (101) , $(10\bar{1})$, $(\bar{1}01)$ and $(\bar{1}0\bar{1})$. This form is also frequently called a dome. The two types of domes are distinguished by their crystallographic symbols. The forms so far described have been of the simplest kind. Prisms are not uncommon which make different intercepts on the a - and b -axes, such as $\{210\}$ and $\{120\}$. In the prism $\{210\}$ the face (210) makes a shorter intercept on the a -axis than on the b -axis, because the indices given in the symbol are the reciprocals of the intercepts, and therefore an index 2 represents an intercept of $\frac{1}{2}$. Similarly domes such as $\{012\}$, $\{021\}$, $\{102\}$ and $\{201\}$ may be found. Many forms with higher indices are known, but they are not very common.

For an orthorhombic crystal all the types of form have been considered which cut one axis or two axes, and it only remains to describe the type of form which intersects all three of the crystallographic axes. A form like the illustration of Fig. 1/10 is called a bipyramid, as it is doubly terminated, like two simple pyramids base to base. The form illustrated has the symbol $\{111\}$. It has the same axial ratios as all the earlier drawings. An orthorhombic bipyramid is

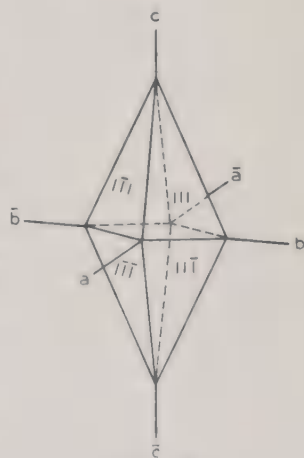


Fig. 1/10.

an eight-faced form. Bipyramids with other symbols may occur, such as $\{211\}$, $\{112\}$, $\{121\}$, $\{311\}$ etc.*

4. Crystallography of Sucrose

DR. A. F. SEAGER

Crystals of sucrose belong to the monoclinic crystal system. In this system there are three unequal crystallographic axes, two of which are at right-angles while the third is inclined. In the conventional orientation, in which an observer is supposed to study the crystal, the c -axis is vertical, the b -axis is horizontal and runs from left to right, while the a -axis is inclined downwards from back to front (Fig. 1/11). The latter axis is therefore at rightangles to the b -axis, but is inclined to the c -axis. The positive and negative ends of the axes are the same as in the orthorhombic system, illustrated in Fig. 1/1, and shown also in Fig. 1/11.

In the monoclinic system there are three classes of symmetry. The most symmetrical class (holosymmetric class) possesses an axis of two-fold sym-

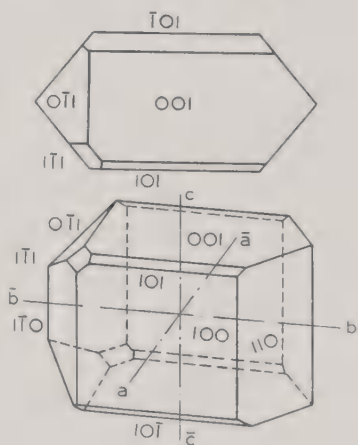


Fig. 1/11.

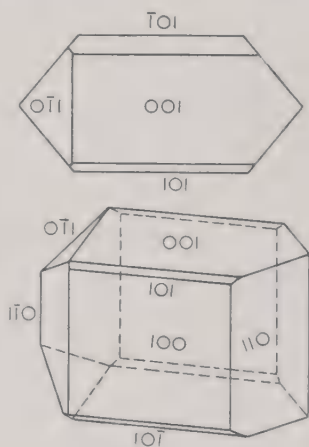


Fig. 1/12.

metry, which coincides with the crystallographic b -axis, a plane of symmetry normal to this axis, and hence coinciding with a possible face (010), and a centre of symmetry. Of the two less symmetrical classes one (the domatic class) has only a plane of symmetry, which is parallel to (010), and the other (the sphenoidal class) has only an axis of two-fold symmetry, which coincides with the b -axis.

* This account of crystal morphology and the determination of indices has been made short and simple deliberately. Formal descriptions of the determination of axial ratios and indices have been omitted. Likewise, names have been given to few forms, as a confusing diversity exists in the literature. For those wishing to pursue 'classical' crystallography further, an excellent textbook is *An Introduction to Crystallography* by F. C. PHILLIPS, published by Longmans, Green & Co., London, 1946.

It is now necessary to decide to which of the three monoclinic classes sucrose belongs. Evidence of several kinds is available on which a decision can be based. The first evidence to be studied is usually the symmetry displayed by the forms developed on the crystals. This kind of evidence may or may not lead to a unique solution. If a crystal belongs to one of the less symmetrical classes and develops forms exhibiting the full symmetry of its class, this information alone can be used to decide the class. A crystal may not, however, necessarily develop such forms, in which case other lines of enquiry must be made. Even if the forms developed by the crystal seem to indicate its true symmetry clearly it is still most desirable to corroborate the conclusion with other tests.

In the drawings of sugar crystals (Figs. 1/11 to 1/22) it will be seen that many of the crystals have a pair of inclined faces at the left hand end, the faces $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$. In only one case is a similar pair of faces seen at the right hand end of the crystals, in Fig. 1/13, and even then they are smaller than the corresponding faces on the left. A pair of small, rarely developed faces is also seen on the top front left and lower back left corners in Fig. 1/11. They are the faces $(1\bar{1}1)$ and $(\bar{1}\bar{1}\bar{1})$. This face development strongly suggests a lateral asymmetry in crystals of sucrose. This is borne out by three further observations. On the large Kandi crystals grown supported on a thread

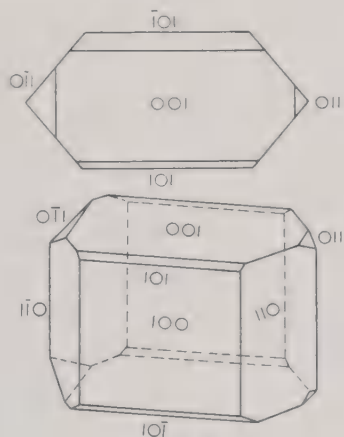


Fig. 1/13.

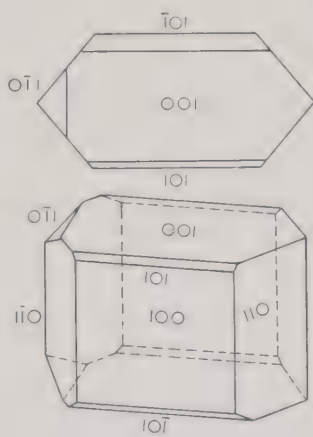


Fig. 1/14.

it may be seen that the centre of the thread within the crystal is to the left of the centre of the crystal in the customary orientation. This is not always clear in every crystal, but if a large number are examined it is obviously true for the majority. This indicates that the crystal grows rather more rapidly to the right of its centre than to the left. Again, if newly-grown crystals are examined, which are untouched by hand, it will be seen that the left hand vertical (prism) faces have a higher lustre and are more smooth or plane

than the corresponding faces at the right hand end of the crystal. Finally, if the same four faces are etched, by subsection to very slight solvent action, the minute etch-pits which are developed have a different shape on the left hand pair of faces to those found on the right.

All the observations mentioned in the last paragraph point to the same conclusion, that there are certain physical differences between the left and right hand ends of the crystal. This is enough evidence to prove the class of symmetry to which sucrose belongs. Of the three classes of symmetry belonging to the monoclinic system the first two mentioned above possess a plane of symmetry. This plane is at rightangles to the b -axis and parallel to a possible face (010). When such a plane of symmetry is present, the left and right hand ends of the crystal should show the same face development, in a perfect crystal, and should be identical in all other properties. We may therefore deduce that sucrose belongs to the sphenoidal class of the monoclinic system, in which the only symmetry element is an axis of twofold symmetry, and there is no plane or centre of symmetry. This conclusion may be confirmed by a study of the optical properties of sucrose. Sucrose crystals are optically active, causing the plane of polarised light to be rotated when a beam is propagated parallel to either of the optic axes. This property is to be expected in crystals belonging to the sphenoidal class, but not in those in either of the other two classes of the monoclinic system.

Some of the crystallographic constants of sucrose will now be given.

Axial ratios, $a : b : c = 1.2595 : 1 : 0.8782$.

The axial angle β , between the a - and c -axes is $103^\circ 30'$.

From these constants it is possible to calculate the interfacial angle between any pair of faces on the crystal. Table 1 below gives the interfacial angles (measured as the angles between the normals to the faces) for the faces which commonly occur on crystals of sucrose.

TABLE 1
INTERFACIAL ANGLES OF SUCROSE CRYSTALS

Pair of Faces	Angle
($\bar{1}01$) (001)	$39^\circ 00'$
(001) (101)	$30^\circ 15'$
(101) (100)	$46^\circ 15'$
(100) ($10\bar{1}$)	$64^\circ 30'$
(100) (110)	$50^\circ 46'$
(001) ($0\bar{1}1$)	$40^\circ 30'$
(101) ($1\bar{1}1$)	$32^\circ 24'$

Now that the symmetry has been determined it is possible to describe the forms developed on crystals of sucrose. A form is a set of crystallographically equivalent faces; if one face of a form is present the rest of the set is, theoretically, demanded by the symmetry. Since the only element of symmetry in sucrose is an axis of twofold symmetry all forms will consist of two faces only, related to each other by a rotation of 180° about the axis of symmetry. There is a (theoretical) exception to this statement, for a possible face or faces at rightangles to the axis of symmetry. One could occur at each end of the crystal, that on the right of the crystal having the index (010) and that on the left $(0\bar{1}0)$. If a face at rightangles to the axis of symmetry is rotated through 180° no new plane is developed, therefore the faces (010) and $(0\bar{1}0)$ are independent of each other and each is a separate one-faced form. These two forms have not yet been recorded on sucrose. With these exceptions all forms on sucrose consist of two faces. When a face is parallel to the axis of symmetry, as many are, the form will comprise a pair of parallel faces.

The drawings of sucrose crystals in Figs. 1/11–1/17, 1/21 and 1/22 represent idealised drawings of the various habits the author was able to find when he had the opportunity of studying a collection of seventy crystals of sucrose, most of which measured one to one and a half inches in length. Except for the left-hand half of Fig. 1/22, the drawings are idealised in the sense that both faces of a form are represented as being the same size. Owing to certain vicissitudes of growth this is often not the case on real crystals, in fact it is not uncommon in sucrose to find that only one face of a form is actually developed. Figs. 1/18 to 1/20 illustrate habits not represented in the collection mentioned above, but are new drawings of habits described in the literature. In Figs. 1/11 to 1/21 the upper drawing is a plan view, or projection along the c -axis, while the lower drawing is a

TABLE 2

FORMS COMMONLY DEVELOPED ON CRYSTALS OF SUCROSE

Letter Symbol	Miller Symbol of Form	Miller Symbol of Faces in Form
a	$\{100\}$	$(100), (1\bar{0}0)$
c	$\{001\}$	$(001), (00\bar{1})$
p	$\{1\bar{1}0\}$	$(1\bar{1}0), (11\bar{0})$
p'	$\{110\}$	$(110), (1\bar{1}0)$
d	$\{101\}$	$(101), (1\bar{0}1)$
r	$\{10\bar{1}\}$	$(10\bar{1}), (101)$
q	$\{0\bar{1}1\}$	$(0\bar{1}1), (01\bar{1})$
q'	$\{011\}$	$(011), (0\bar{1}1)$
o	$\{1\bar{1}1\}$	$(1\bar{1}1), (11\bar{1})$

front view, in which the crystal is rotated slightly clockwise and has a small tilt forward. In Fig. 1/22 the forward tilt has been omitted in the lower drawing in order to show the $(00\bar{1})$ face of that part of the twin crystal which is in reverse orientation.

Table 2 gives the letter symbols commonly used to refer to the forms on crystals of sucrose, together with the Miller symbol of the form, and of the two faces which comprise each form.

Of these forms the least common are certainly $\{1\bar{1}1\}$ and $\{011\}$. Most of the others occur on the majority of crystals, but $\{0\bar{1}1\}$ and $\{101\}$ are not infrequently absent. $\{0\bar{1}1\}$ is missing in Figs. 1/15 and 1/21, while Fig. 1/16 shows how $\{001\}$ may grow at the expense of $\{101\}$, even causing its

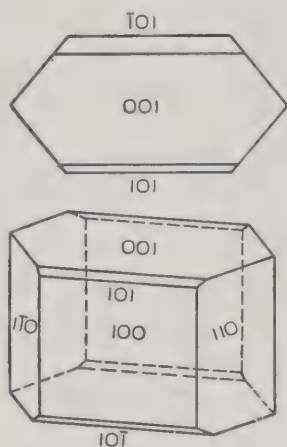


Fig. 1/15.

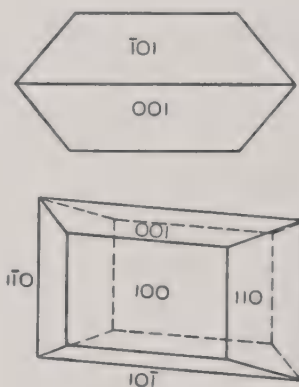


Fig. 1/16.

elimination. On the majority of crystals $\{100\}$ is the largest form, and the crystals are usually slightly flattened or tabular in this direction. Occasionally the flattening becomes pronounced, and the crystals are markedly tabular on $\{100\}$, as shown in Fig. 1/21. This tabular habit is also characteristic of the twin crystals in the collection studied, as illustrated in Fig. 1/22. One crystal showed a distinct trend away from the flattened habit, being relatively much thicker in the direction of the a -axis (Fig. 1/17). Sometimes

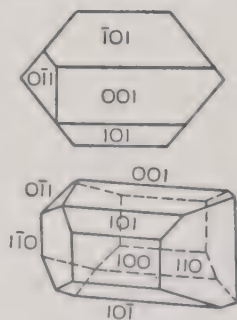


Fig. 1/17.

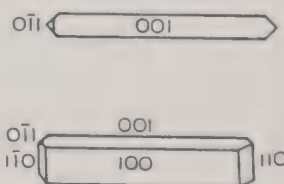


Fig. 1/18.

elongated habits occur. The acicular or needle-like habit of Fig. 1/18 shows a crystal elongated on the b -axis by the prominent development of $\{100\}$ and $\{001\}$. The crystal of Fig. 1/19 is elongated on the c -axis by the prominent development of $\{110\}$ and $\{1\bar{1}0\}$. Fig. 1/20 shows an unusual

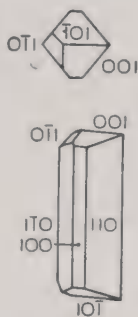


Fig. 1/19.



Fig. 1/20.

triangular crystal formed by the dominance of $\{0\bar{1}1\}$, which is here so exaggerated that $\{001\}$, $\{101\}$ and $\{10\bar{1}\}$ are completely eliminated.

The last drawing represents a twin crystal (Fig. 1/22). When many crystals are grown in one vessel it is not uncommon for various kinds of aggregates

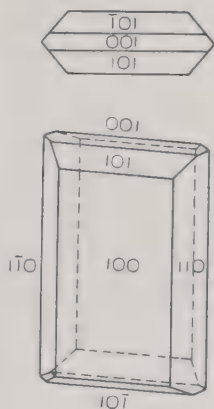


Fig. 1/21.

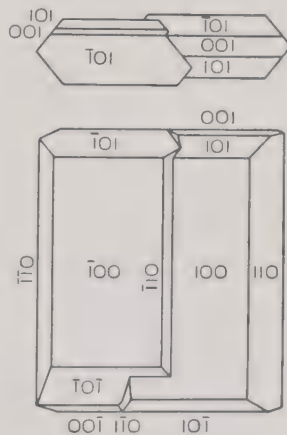


Fig. 1/22.

to be formed. Most aggregates are of a random character, two or more crystals growing into each other in chance orientation, often due to overcrowding. But there are several kinds of ordered aggregate which may occur in crystals, when two or more individuals intergrow according to definite geometrical laws. The simplest type of aggregate is formed in

parallel growth. In this case two or more crystals grow upon each other with their respective crystallographic axes and corresponding edge directions all parallel. A more complex type of intergrowth is found in twin crystals, in which two or more individuals intergrow according to definite geometrical laws, which are closely connected with the symmetry of the crystal concerned. The orientation of one part of the twin with respect to the other is related either by reflection across a plane or by a rotation of 180° about an axis or by both processes. The plane and axis used to describe twinning are called a twin plane and twin axis. The twin plane cannot be parallel to a plane of symmetry in the untwinned crystal, and a twin axis cannot coincide with an axis of symmetry of even degree in the untwinned crystal, that is one of twofold, fourfold or sixfold symmetry. Thus a twin axis may be parallel to an axis of threefold symmetry, or it may not coincide with any axis of symmetry.

In sucrose the twinning can be described as due to reflection across a twin plane parallel to the face (100). Consider a crystal of the habit of Fig. 1/21. This forms the right-hand part of the twin shown in Fig. 1/22. Now visualise another crystal, in front of the right-hand part, which is a mirror image of that part across a plane parallel to the face (100), so that both parts have their (100) faces in contact. These two crystals are now in twin orientation, they are said to be twinned on the plane (100), as this face is the twin plane. The two crystals are mirror images of each other across the twin plane. In other words, if one of the crystals is removed and a mirror put in its place, parallel to (100), the crystal and its mirror image will appear to occupy the positions of the two single crystals before one was removed. The above description indicates the relative orientation of the two parts of the twin of sucrose, but not their mode of attachment. The parts of a twin may interpenetrate irregularly, or they may be attached on a plane or nearly plane surface. In the case illustrated the crystals are united as though the face (0 $\bar{1}$ 0) of the right-hand part was in contact with the (010) face of the left-hand part.

The right-hand part of this twin is shown in the usual orientation, with the faces (101) and (001) appearing in the front at the upper part of the crystal. The left-hand part of the twin is inverted with respect to the right-hand part. The left-hand part is indexed as though it had been reflected across the plane (100). Its upper face is ($\bar{1}$ 01), which is the symbol of the upper face at the *back* of the right hand part. (Only the front faces of the drawings have had symbols placed on them. If any difficulty is experienced in determining the symbols of the back faces it may be of assistance to realise that parallel faces have exactly the same numerical symbols but with

all signs reversed. In most of the drawings, where undue complication is not introduced, the back faces have been shown. Thus the opposite face to (100) is $(\bar{1}00)$, of (101) it is $(\bar{1}0\bar{1})$. This method is applicable in cases, where, as in some faces on sucrose, the parallel faces even belong to different forms; for example the parallel face to (110) is $(\bar{1}\bar{1}0)$, and for (011) it is $(0\bar{1}\bar{1})$. The reason for this rule is that parallel faces must cut the opposite ends of the same axes.) The remaining faces whose symbols are given on the front of the left-hand part will be found at the back of the right-hand part of the twin.

(a) *Crystallographic Zones*

A zone in crystallography is a group of faces which are all parallel to one line, which is called the zone-axis. The faces of one zone meet each other in parallel edges, which are themselves parallel to the zone-axis. In some cases it is necessary to produce the faces to cause them to meet other faces in the zone. Nearly all the crystals of sucrose illustrated have two very prominent zones. In one case the b -axis is the zone-axis, and in Fig. 1/11 to 1/15, for example, there are eight faces in this zone, composed of a pair of faces of each of the forms $\{100\}$, $\{101\}$, $\{001\}$ and $\{10\bar{1}\}$. It will be observed that in each of these symbols the middle index is a nought, indicating that the face is parallel to the b -axis. The other well developed zone has the c -axis as zone-axis. This zone, containing six faces, is to be found on every one of the twelve drawings of sucrose. The three forms in this zone are $\{110\}$, $\{100\}$ and $\{1\bar{1}0\}$. It will be noticed that in this case the third index of each form is a nought, indicating that all the faces are parallel to the c -axis, and the edges between the faces are also parallel to that axis. Another zone of six faces may be seen in Fig. 1/13, consisting of the forms $\{011\}$, $\{001\}$ and $\{0\bar{1}1\}$. In this case parallel intersections may be seen between the faces (011), (001) and $(0\bar{1}1)$ on the top of the crystal, and also between the three opposite parallel faces in the lower part of the crystal. In this particular crystal there are no edges parallel to the zone-axis between the faces (011) and $(01\bar{1})$ or between $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$. These are examples of faces which have to be produced before an intersection may be obtained. The last zone described has the a -axis as zone-axis, and all faces falling in this zone have a nought for the first index.

Each of the zones mentioned above had its zone-axis parallel to one of the crystallographic axes. Any further zones which may be found on the crystal will have their zone-axes oblique to the crystallographic axes. In such cases it will not be possible to find the zones by observing the position of noughts in the indices. In the Figs. 1/13 and 1/14 there is a well developed

zone parallel to certain prism edges, comprising the faces (001) , $(\bar{1}10)$, $(00\bar{1})$ and $(1\bar{1}0)$. In Fig. 1/15 there is in addition to this zone another similar one containing the faces (001) , (110) , $(00\bar{1})$ and $(\bar{1}\bar{1}0)$. In the crystal of Fig. 1/11 other zones may be found including faces of the form $\{1\bar{1}1\}$. In general a zone may be defined by the intersection of any two non-parallel faces on a crystal.

Zones have several interesting and useful properties. The symbols of faces lying in one zone are simply related to each other by an addition scheme. Consider the symbols of three adjacent faces in one zone. The symbol of the middle face can be obtained by adding n times the symbol of the face on one side of it to m times the symbol of the face on the other side, if account is taken of algebraical sign. In the majority of cases n and m are both unity, particularly on crystals of simple habit or form development like sucrose, but it is not safe to assume a value of unity. To take an example: on many of the crystals of sucrose a narrow face replaces the edge between the faces (100) and (001) . These symbols should be added, index to index, for the a -, b - and c -axes, respectively, as follows

$$\begin{array}{r} 100 \\ 001 \\ \hline 101 \end{array}$$

In this case (101) is the correct symbol of the face. When (110) and $(1\bar{1}0)$ are similarly added the symbol of the front face (100) is obtained. Conversely this method may be used to ascertain if three faces do actually lie in the same zone. If the addition of the symbols, or any integral multiple of them, gives the symbol of the intermediate face, then those faces belong to the same zone.

On some crystals the certain determination of indices can be accomplished by the use of zone-symbols. A zone-symbol may be calculated from the symbols of any two faces in a zone which are not parallel. Let the symbols of two faces be (hkl) and (pqr) , and the zone-symbol, which is enclosed in square brackets, be $[uvw]$. The symbol of the zone is found by cross-multiplying the symbols of the faces in the following manner. The symbol of one face is written above the other, each symbol

$$\begin{array}{c|ccc|c} h & k & l & h & k & l \\ & \times & \times & \times & & \\ p & q & r & p & q & r \end{array}$$

being repeated. Two vertical lines are drawn to indicate that no use is made of the end index of each row. The value of u is found by multiplying

the two indices joined by the first diagonal north-west to south-east stroke, k and r , and subtracting from them the product of the indices joined by the cross stroke, l and q . Proceeding in a similar manner $v = lp - hr$ and $w = hq - kp$. The zone-symbols will now be calculated for some of the zones common on crystals of sucrose. The best developed zone, containing (100) and (001) will be taken first.

$$\begin{array}{c|cccc|c} 1 & 0 & 0 & 1 & 0 & 0 \\ & \times & \times & \times & & \\ 0 & 0 & 1 & 0 & 0 & 1 \end{array} \quad u = (0 \times 1) - (0 \times 0); v = (0 \times 0) - (1 \times 1); w = (1 \times 0) - (0 \times 0).$$

Hence the zone-symbol $[uvw]$ is $[0\bar{1}0]$. If, when cross-multiplying, the symbol (001) had been placed above that of (100) the zone-symbol would have been $[010]$, the same symbol, but of opposite sign. This indicates that the sign is of little importance, the sign of all three integers may be changed without affecting the significance of the symbol, but it is not permissible to alter the sign of one or two integers only. The reason stems from the significance of the zone-symbol. It is a set of co-ordinates defining the direction of the zone-axis with respect to the crystallographic axes. If it is imagined that the zone-axis passes through the point at which the three crystallographic axes meet, then the zone-symbol defines another point on the zone-axis, and hence defines its direction. The three crystallographic axes are thus used as a system of coordinates, like a three-dimensional graph. The zone-symbol $[010]$ indicates that the other point which is being defined on the zone-axis is not displaced at all along the a -axis, it is displaced along the b -axis, and it is not displaced along the c -axis. Therefore this other point can only lie on the b -axis. Since the zone-axis also passes through the point of intersection of the three crystallographic axes this zone-axis must coincide with the b -axis. The significance of the zone-symbols $[010]$ and $[0\bar{1}0]$ is that the first symbol defines the other point on the zone-axis on the right-hand side of the crystal, while the second symbol defines it on the left. Since both points lie on the same straight line they both define the same zone-axis. It will be noted that the zone-axis is parallel to the edges between faces lying in the zone.

The zone-symbol for the zone containing the faces (100) and (110) is $[001]$, indicating that the zone-axis coincides with the c -axis, as is evident from the edge-direction of the zone. The zone-symbol for the zone containing the faces (001) and $(0\bar{1}1)$ is $[100]$, so that in this case the zone-axis is parallel to the a -axis.

Zone-symbols are of particular value for two purposes. If the symbol of a face and of a zone are known it is possible to find by calculation whether

that face belongs to the zone. If the symbol of the face is (hkl) and that of the zone is $[uvw]$, then the face belongs to the zone when $hu + kv + lw = \text{zero}$.

Zone-symbols may be used to find the symbol of a face which lies at the intersection of two zones by cross-multiplying the symbols of those zones. Let it be supposed that, in the crystal of Fig. 1/11, the symbols of all the faces are known except for that of the relatively rare face $(1\bar{1}1)$. From the two pairs of parallel edges bounding it, the fact may be deduced that this face lies at the intersection of two zones, one passing through (100) and $(0\bar{1}1)$, and the other through $(1\bar{1}0)$ and (001) . The symbols of both zones must first be obtained. Cross-multiplying (100) and $(0\bar{1}1)$ with the first symbol above gives the zone-symbol $[0\bar{1}\bar{1}]$, and in the second zone, cross-multiplying with $(1\bar{1}0)$ above, the zone-symbol $[\bar{1}\bar{1}0]$ is obtained. When these two zone-symbols are cross-multiplied with $[\bar{1}\bar{1}0]$ above, the face symbol $(1\bar{1}1)$ is derived, which is the correct symbol of the face. If the cross-multiplication of zone-symbols had been carried out with $[0\bar{1}\bar{1}]$ above, the answer would be the face symbol $(\bar{1}1\bar{1})$. This is a face of a form which does not occur on the crystal shown in Fig. 1/11. It will be observed that the face $(\bar{1}1\bar{1})$ has all its signs reversed compared with $(1\bar{1}1)$, and it will therefore be a face parallel to $(1\bar{1}1)$ on the opposite side of the crystal. This type of ambiguity is always possible, but the correct answer can easily be found by inspection.

(b) *The Stereographic Projection*

This is the projection most widely used to represent crystals. Drawings and stereographic projections of crystals are, in a sense, complementary. In a drawing it is possible to represent the shape and relative size of the faces on a crystal, but little information can be readily derived about interfacial angles, the angles between the crystallographic axes or axial ratios. The stereographic projection, on the other hand, gives precise information about interfacial and interaxial angles, and will yield axial ratios, but it gives no indication whatsoever of the shape of individual faces or of their relative development, which determines the habit of the crystal.

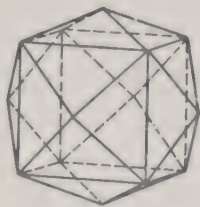


Fig. 1/23.

Fig. 1/23 shows a four-faced cube, which is like a cube on which a low four-faced 'pyramid' has been added to each face. The principle of the stereographic projection is illustrated in Fig. 1/24, in which some faces of the four-faced cube are projected. It is imagined that the crystal is sur-

rounded by a sphere, both having a common centre. The crystal is shown projected along one of its crystallographic axes, and a zone of eight faces, D, G, K, P, T, V, X, Y , is normal to the plane of the paper. The faces in this zone will be projected stereographically. Project the normal to each face until it cuts the surface of the sphere. This point on the sphere is called the 'pole of the face'. For example, DE is the normal to the face D , and E is the pole of that face. Let N and S represent the north and south poles of the sphere. If the pole of a face falls in the northern hemisphere it is joined by a line to the south pole, for example ES , and this line cuts the equatorial plane ABC at F . The equatorial circle ABC , with centre O , shown in the lower part of the figure, is at rightangles to the same circle ABC in the upper part of the figure. The final stereographic projection is made on the equatorial plane of the sphere of projection, hence it is necessary to project F to F' , which is the required point in the projection. Since the face D is normal to the plane $ANCS$ the normal to D lies in that plane, and therefore falls on the line AC in the lower circle. Similarly, the normal to the face G meets the surface of the sphere of projection at H . The line joining H to the south pole cuts the equatorial plane at J , and J' is the point required in the final projection. The remaining faces in the upper hemisphere, K and P , are projected in the same manner. The poles of these faces are found at L and Q and are ultimately projected to M' and R' , respectively. Faces in the lower hemisphere are projected in the same way, except that the poles of the faces are joined to the north pole. The pole of the face T is found at U , and UN , joining the face pole to the north pole, cuts the equatorial plane at F , and is finally projected to F' . The projections of the faces D and T therefore coincide. Similarly the pole of

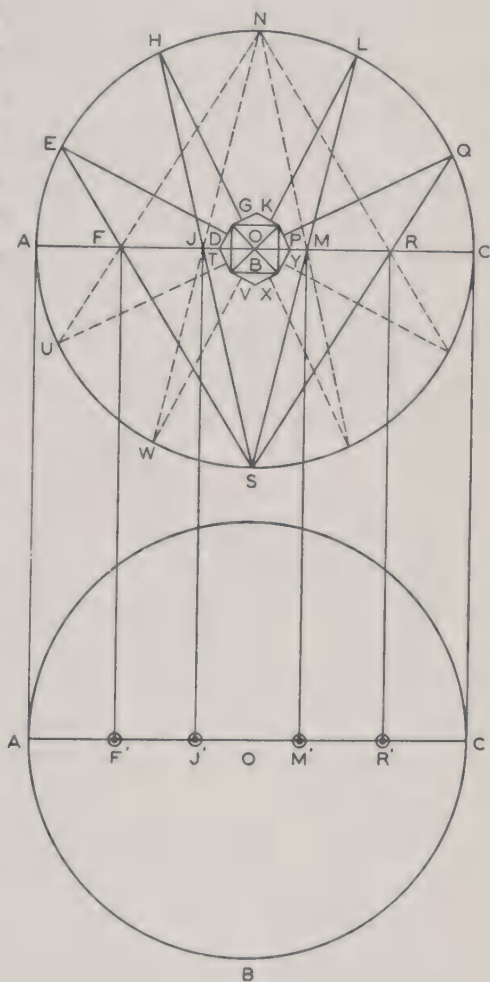


Fig. 1/24.

the face V is at W , and it is projected to J and J' . The remaining faces in the lower hemisphere, X and Y , are finally projected to M' and R' . The faces T , V , X and Y of the lower hemisphere are thus projected to the same points as the faces D , G , K and P , respectively, of the upper hemisphere. The reason for this may be seen from the upper part of the figure. The plane ABC , the equatorial plane, is a plane of symmetry of the crystal. The face D is thus a mirror image of the face T , G is a mirror image of V , and K and P are mirror images of the faces X and Y . Faces related by a plane of symmetry have their poles similarly related to that plane. Thus the faces D and T are mirror images of each other, and their poles E and U are also mirror images across the plane ABC , the former pole falling in the upper hemisphere and the latter in the lower hemisphere. It is the convention in stereographic projections to represent faces whose poles fall in the upper hemisphere by a point or small dot and those falling in the lower hemisphere by a small open circle, as shown in the lower part of Fig. 1/24.

As a further example of making a stereographic projection a cube is illustrated in Fig. 1/25 and its projection in Fig. 1/26, in which the upper and lower circles have

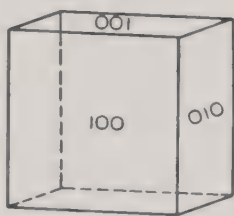


Fig. 1/25.

the same significance and orientation as in Fig. 1/24. GN is the normal to the upper face of the cube, (001), so that the pole of this face coincides with the north pole of the sphere of projection. The line joining N to the south pole passes through the centre of the sphere of

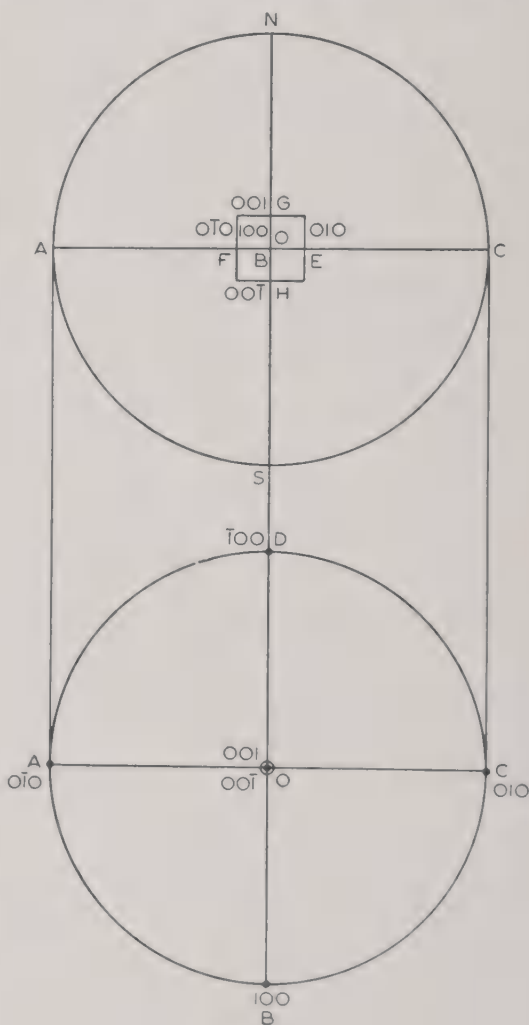


Fig. 1/26.

projection at O , and is therefore shown at the centre of the equatorial plane in the lower part of the figure. The lower parallel face of the cube, $(00\bar{1})$, is projected to the same point, and represented by a small open circle. The right hand side face of the cube, (010) , has its pole at C in the upper part of the figure. This point on the surface of the sphere also lies on the circumference of the equatorial plane, and this is therefore the required point in the projection. The parallel opposite face, $(0\bar{1}0)$, will be projected in a similar manner to the point A . The normal to the front face of the cube, (100) , is OB , which is fore-shortened to a point in the upper part of the figure. OB also lies in the equatorial plane, and therefore B is the required point in the projection. The parallel face at the back of the cube, $(\bar{1}00)$, is projected to D .

When first using the stereographic projection it is not always easy to visualise the shape of a crystal from the distribution of points in a stereogram. Several characteristics of the projection can be deduced from the Figs. 1/24 and 1/26 which may help considerably in the three-dimensional visualisation of crystals. Firstly, when a cube is held in the conventional orientation, the horizontal faces both appear in the centre of the projection. Secondly, the four vertical faces of the cube appear on the circumference of the projection, on what is often called the primitive circle. Moreover, the direction of all vertical faces is given by the tangent to the primitive circle at the point representing the projected face. In the case of the cube the four tangents fall into two pairs which are mutually perpendicular, as are the corresponding faces on the cube.

In the three crystal systems which possess crystallographic axes at right-angles (cubic, tetragonal and orthorhombic systems) the crystallographic axes are orientated in a stereographic projection as in the lower part of Fig. 1/26. The vertical axis of the crystal passes through the centre of the projection normal to the plane of the paper, while the front-to-back and left-to-right axes of the crystal run up-and-down and left-to-right on the page. If a face is parallel to an axis the normal to that face will also be normal to the axis. Thus faces lying parallel to the front-to-back axis, as D , G , K , P , etc. in Fig. 1/24, will appear, in projection, along the left-to-right axis, and vice versa.

It has now been shown that a horizontal face lies in the centre of the projection and a vertical face on the circumference. From Fig. 1/24 it will be seen that for inclined faces the steeper is their slope the nearer the circumference do they appear. The inclined face D is relatively steep and appears in projection at F' , while the shallower face G is projected nearer the centre at J' . Thus a face which is projected on the left-to-right line

The other method of projection used for monoclinic crystals, shown in Fig. 1/28, is similar to that used for crystals in which the crystallographic axes are at rightangles. The c -axis is placed vertical and the b -axis runs horizontally from left to right. The trace of the a -axis is along the line joining the faces (100) and $(\bar{1}00)$, but the axis is not normal to these faces, as may be seen in Fig. 1/27. In this projection (Fig. 1/28) all faces parallel to the c -axis will appear on the primitive circle. Since the face (001) is not at rightangles to the c -axis, it will not appear in the centre of the projection, but forward of that position, to indicate its forward tilt. The face $(00\bar{1})$ will be displaced a similar distance behind the centre. The possible face (010) would appear on the primitive circle at the right-hand end of the b -axis, and $(0\bar{1}0)$ at the opposite end of the same diameter. The approximate position of other faces can then be found by use of the addition scheme of indices. All the faces parallel to the b -axis will lie on the line at rightangles to it, only leaving the forms $\{0\bar{1}1\}$, $\{011\}$ and $\{1\bar{1}1\}$ to be found. The face $(0\bar{1}1)$ will lie on the zone-circle (projected arc of an inclined great circle of the projection, which passes through faces of one zone) joining the faces (001) and $(0\bar{1}0)$, while (011) will lie between (010) and (001) . The face $(1\bar{1}1)$ will lie on the zone-circle containing (101) and $(0\bar{1}0)$ and also on the zone-

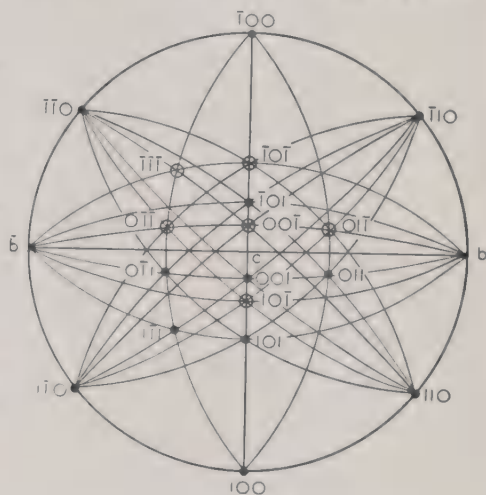


Fig. 1/28.

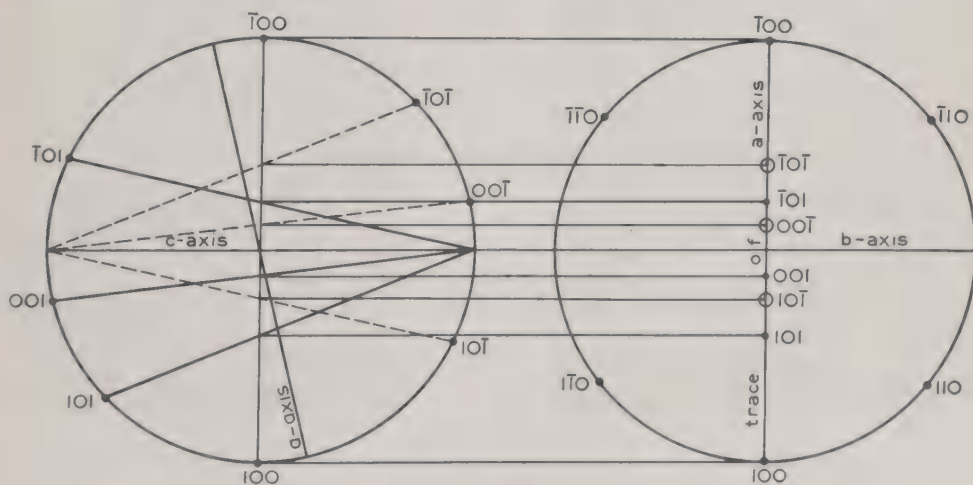


Fig. 1/29.

circle passing through (100) and (0 $\bar{1}$ 1). Many other zone-circles have been shown in this figure, indicating the large number of zones which may be found on even fairly simple crystals.

The relationship between the projections used in Figs. 1/27 and 1/28 is illustrated in Fig. 1/29. The left-hand circle shows the vertical faces of

Fig. 1/27, those which appear on the primitive circle. The right-hand circle shows the faces of the same zone (and a few others for reference) as projected in Fig. 1/28. It has been necessary to rotate the left-hand circle 90° compared with its orientation in Fig. 1/27 in order to bring out the relationship between the projections. In the left-hand circle the faces on the primitive circle have been joined to the pole of the opposite hemisphere. The points at which these lines cut the equatorial plane are the required points for the projection of these faces in the right-hand circle, as may be seen by the horizontal lines joining the two circles.



Fig. 1/30, 1/31, 1/32. Kandi crystals exhibiting three stages in the relative development of faces 101 and 001. Selected from a number presented to the author by Messrs. PFEIFFER and LANGEN.

5. Forms of Sucrose Crystals

Illustrations 1/30–1/34 show how widely the apparent form of sucrose crystals may vary. For a study of the morphology of sucrose crystals, large size sucrose crystals can be used for demonstration purposes, and particu-



Fig. 1/33. Needle form of sucrose from low quality refined sugar boiling, not caused by raffinose.



Fig. 1/34. Triangular or pyramidal form of sucrose, reproduced by the courtesy of the 'Institut für Zuckerindustrie', Berlin.

larly for educational purposes to familiarize sugar technologists with the exact structure of the sucrose crystals. Kandi crystals as given in the Figs. 1/30–1/32 are the most useful objects for this purpose. This type of crystals can be kept indefinitely, if they are inbedded in one of the modern plastics, which can easily be done by a sugar technologist in the laboratory. Abnormal shapes of sucrose crystals as illustrated in Fig. 1/33 and 1/34 can also be kept in the same way embedded in plastic, and either used for projection to demonstrate on a large scale for a big audience the particulars of these crystal forms or the particulars can be laid down in microphotographs, accompanied by detailed drawings of the different surfaces to be distinguished at these crystals, with the indications of the type of surface as described in the preceding paragraphs.

So far we have been considering essentially normal single crystals, but every sugarman is familiar with so called twinned crystals (see Fig. 1/35–1/39), wherein two or more crystals appear to have a common bond. The phenom-

enon does not appear to have received systematic study in the specific case of sucrose, though VON LIPPMANN and VAVRINECZ⁹ give a number of valuable observations. VAVRINECZ suggests using the symbol π to signify the ratio $\frac{\text{height or length}}{\text{breadth}}$ of twins, thereby giving simple numerical expression to their outward form; he records π varying from 1.59 to 6.12.

It may be helpful to quote evidence from the study of other crystalline substances.

Essentially twinning in crystals implies that two crystals share a common face or edge, *i.e.* either a two dimensional or a one dimensional link. It implies that the harmony of transition from each molecule on to its neighbour may be carried on from the one to the other section of the twin, through the common bond. Thus two adjacent Kandi crystals grown together on a string, or two adjacent crystals in cube sugar are not twins. Be deduction, it would appear that one twin must have grown out of the other by some impulse of irregular growth, very likely even from 'birth'

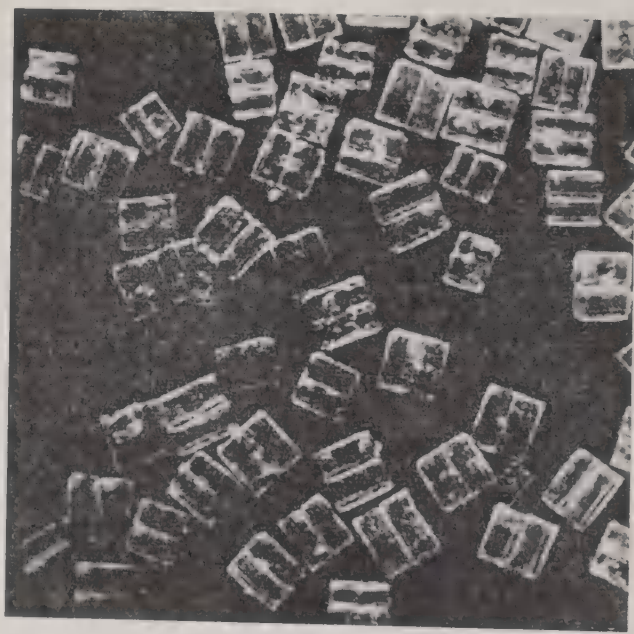


Fig. 1/35. Refined sugar X5. A remarkably uniform twinning.

or nucleation. Re-entrant angles on a crystal are generally an indication of twinning, but twinning may be present without re-entrant angles.

It is evident that two crystals may fulfill the above condition in many ways; some of the well recognised forms are 'normal twins' which share a common plane, which may be: (a) simple mirror images; this is termed a

symmetric twin; (b) one twin having apparently been rotated about the common axis with relation to the other, this is termed a hemitrope. Far more rare are ‘parallel twins’ which share one common crystal edge only, and ‘complex twins’ which share a common line normal to a crystal edge.

An entirely different occurrence is known as interpenetrant twinning,

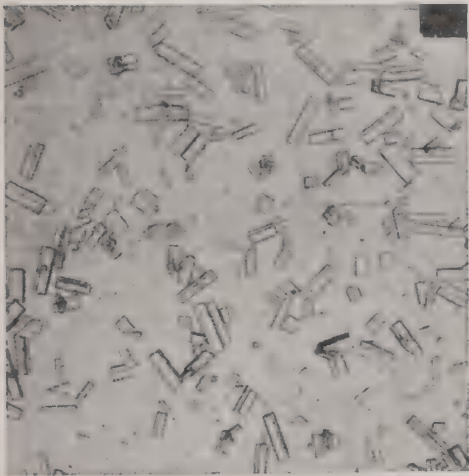


Fig. 1/36. Low quality boiling, showing unbalanced twins.

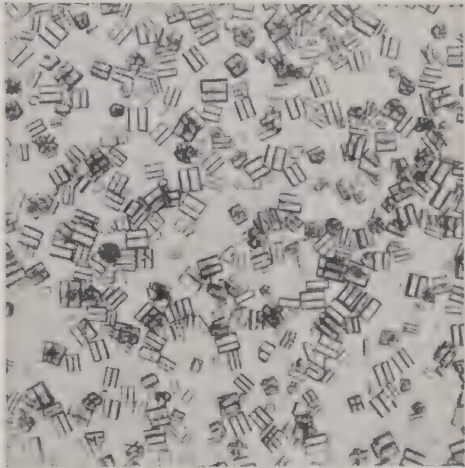


Fig. 1/37. Low quality boiling, showing balanced twins and conglomerates.

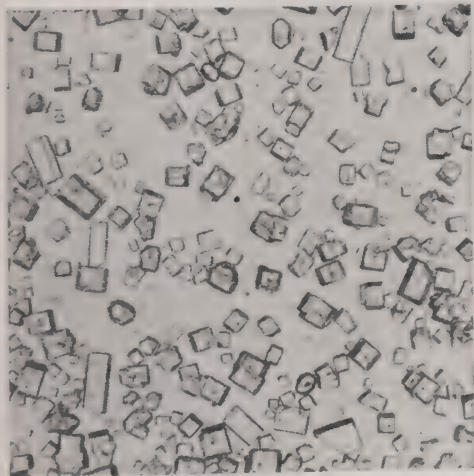


Fig. 1/38. Low quality boiling, showing several types of twins and stained heart.

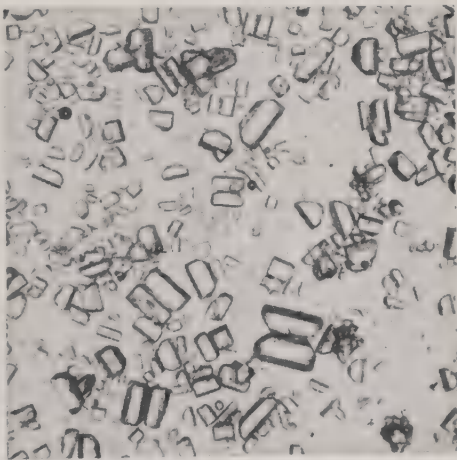


Fig. 1/39. Low quality boiling, showing twinning with exaggerated re-entrant angles.

in which the two crystals appear to be sharing some part of their body. This form is most disconcerting to those requiring crystals for piezo-electric work, necessitating elaborate X-ray testing of apparently perfect crystals in order to detect such internal intrusion.

Twinning is met most frequently in the monoclinic and orthorhombic systems, hence its frequency with sucrose is quite natural. The reason for twinning is not yet completely understood. The subject deserves more study than it has yet received. The study of the junction between the sections of a complex crystal may teach us more about the cause and effect of these mother liquor holding monstrosities as are all too common in our sugar products.

In examining a large number of crystals, one feels the need for a suitable terminology to enable an objective descriptive terminology of the degree of complexity. The term 'cluster' may be used where the crystal conglom-

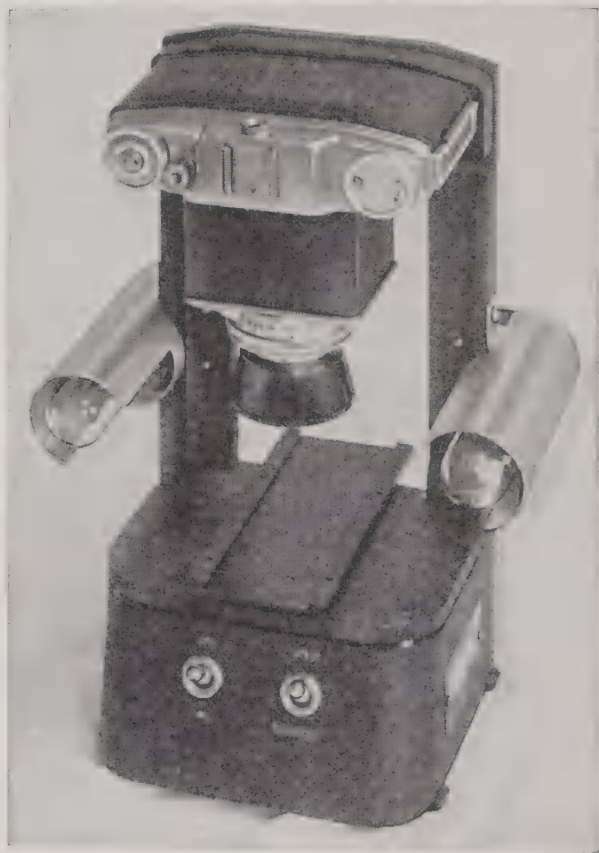


Fig. 1/40. Crystal camera.

erate includes several well formed crystals, and the term 'aggregate' where a starry mass of crystals are implied. The latter form is characteristic of sugars which have been nucleated at too high a supersaturation. This may be the direct result of a dendritic nucleation. A sugar product with a high proportion of such conjoined crystals must necessarily hold mother

liquor in the crevices between the crystal surfaces and render less efficient the separation of the mother syrup from the crystals in the centrifuges. Another feature of potential value is that the volume occupied by a given weight of conglomerated crystals is more than for the same weight of well-formed single sugar crystals, which to the practical man indicates potential saving in packaging material by boiling clean grain. So in fact, the sales department should choose which it prefers, and it should be the effort of the technologist to learn how best to boil sugar in the chosen form.

In the case of low quality boilings, where efficient separation is of major importance, it is fortunately relatively easy to boil good well formed grain, since crystal growth is slower than in high purity boilings and the panman has a less critical task. The purer the massecuite, the more difficult this becomes; it is exceptional in all refineries of the world to have first quality boilings with complete freedom from aggregates and clusters. A number of photographs of sugar grains, to be discussed later, illustrate the simpler forms which may be noted in sugar boilings. The technologists responsible for production of the different grades of commercial sugar can benefit by a detailed study of the form of the crystals produced. Having visited a large number of sugar producing plants, it has to be stated that a visit to the pan floor, armed with a magnifying glass, can be one of the most informative means of obtaining insight into the type of control reigning in that factory or refinery. Low power magnification is quite sufficient for most purposes. I have designed a 'crystal camera' (Fig. 1/40) with which adequate lifesize photographs may be obtained on 35 mm film. Enlargements or projections of these may be shown in demonstrations, lectures or training courses to operatives to illustrate the relative merits of different boilings and techniques. A faulty boiling which wastes time and efficiency in the centrifuge can be easily so recorded.

Occasionally false grain will form in low quality boilings, but it may be suspected that some of the grain is not sucrose but some other intruding crystalline substance. How shall we identify such crystalline impurities? Mineralogists have developed accurate methods for identifying unknown small crystals under the microscope without sacrificing them into solution, by utilising the specificity of refractive index. This deserves a brief mention, since it enables the chemist to identify minute crystals present in liquor and molasses, which not infrequently do occur. The method depends upon having available a series of liquids of differing refractive indices, covering the desired range in jumps of about 0.005 R.I. at room temperature (15–20° C). This product can be analysed as follows. The impurities have to be separated from the liquid sugar product, which can be done in a separator.

These insoluble impurities have always a specific gravity larger than the specific gravity of the sugar liquor or molasses. The sugar product is diluted to a concentration slightly below the saturation value. This is approximately 67 to 72 brix.

The separated sediment is first washed with a saturated solution of high

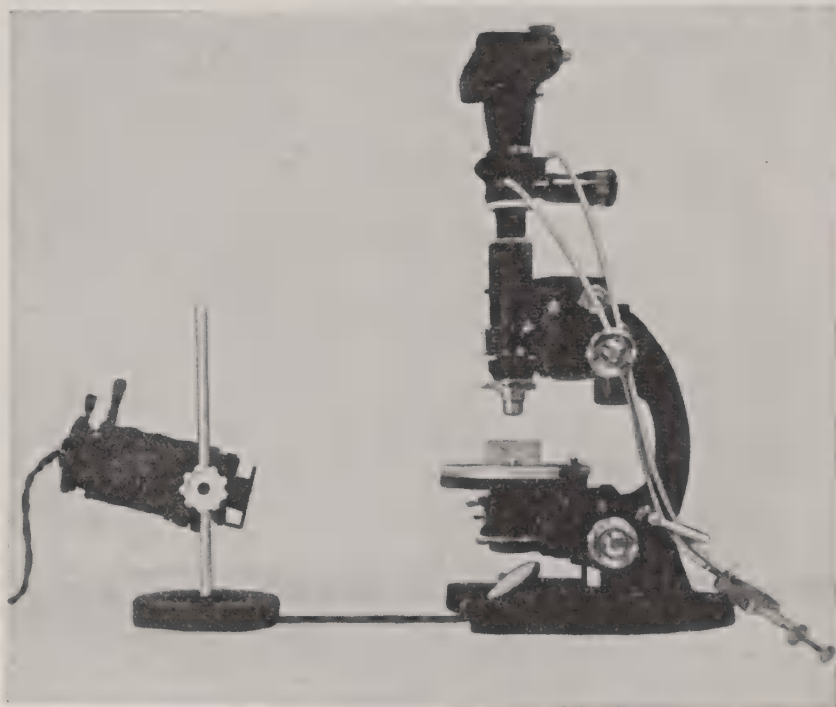


Fig. 1/41. Equipment as used for microphotographs.

grade refined sugar by resuspending the sediment in the solution then reseparating. The precipitate is washed with acetone water v/v 50/50 then dried. The solid matter is then immersed in a series of fluids of increasing and known refractive index and examined under a microscope using low power magnification. The more invisible the crystals, the closer is their refractive index to that of the fluid. In this way the Ca-Mg aconitate, CaSO_4 , Ca-oxalate and CaSO_3 can easily be identified.

6. Physical Properties and Internal Structure of Sucrose Crystals

It is surprising to learn the variations in the specific gravity of sucrose crystals. KUCHARENKO⁴ quotes a variation from 1.5777 to 1.5889; other investigators have given figures even beyond this range. This variation has been demonstrated by POWERS (at the C.I.T.S. Conference in Madrid

in 1954) by adding a random selection of pure sucrose crystals to a mixture of carbon tetrachloride and acetone with a specific gravity of $1.585 \pm$ in a glass stoppered bottle and mixing thoroughly; some of the crystals remain suspended, whilst others rise or fall according to their gravity. The writer has now (1957–1958) been able to prove that this is largely due to the inclusion of air and liquor in the crystal, and two selected crystals gave maxima and minima of 1.594 and 1.582 S.G. Evidence is due for publication B.S.C. Conference 1958.

One often hears the expression 'hard' and 'soft' sugar used by practical sugar technologists; the scientific use of these words 'hard' and 'soft' for the physical characterisation of sucrose crystals is meaningless, as has been well expressed by MCGINNIS* who says, the operator refers to the 'feel' of the grain between the fingers, and that 'soft grain' easily 'rubs out' whilst 'hard grain' feels like little glass particles when so treated. It is therefore probably due to a state of aggregation.

Knowing what variations may occur with sucrose, a number of estimations were made of the surface hardness of different crystals. The results are that there does not appear to be any significant difference in hardness on the corresponding face of different crystals, though there is a marked difference of hardness on different faces of the same crystal. The following two sets of mean results have been obtained by two different laboratories; Prof. S. TOLANSKY intends to carry out some investigations on this subject. The brittle easily cleaved surface of the crystal is not conducive of accurate measurement.

Table 3 gives the mean of a number of estimations.

Face	Lab. I Crystals VHN*	Lab. II Crystals VHN*
100	48	62
$\bar{1}10$	47	37
$\bar{1}00$	58	79
$\bar{1}\bar{1}0$	54	57
$1\bar{1}0$	56	55
$00\bar{1}$	53	73
* VHN = Vickers Hardness Number.		

My early attempts to estimate hardness in a different way, by measuring the pressure necessary to crush a crystal, demonstrated the structure reminiscent of slate. Pressure lengthwise (parallel to the 100 face) caused a splitting parallel to the 100 face, and by the expedient of using a knife

* *Beet Sugar Technology*, Reinhold Publishing Corp., New York, 1951, p. 351.

applied in the right manner, a sucrose crystal may easily be cleaved into a series of parallel flakes. Pressure applied at right angles to this cleavage plane led to disintegration and more or less formless crushing. This is not uncommon in crystallography; it is associated with the position of the molecules in the crystal lattice. When a crystal is crushed by applied force,

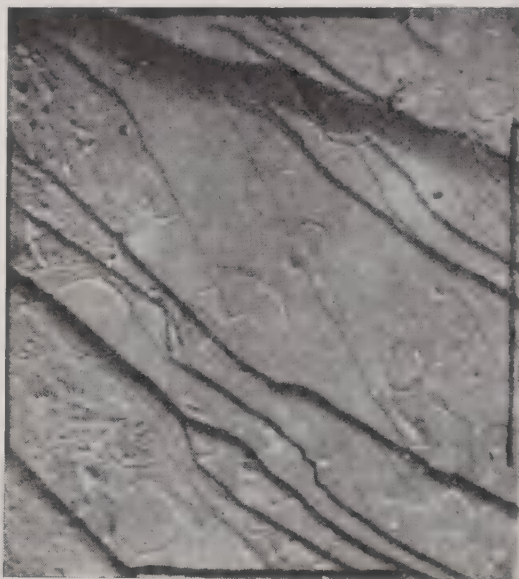


Fig. 1/42. Electron micrograph of cleaved surface of sucrose crystal ($\times 20,000$).

some of the molecules are forced apart, in spite of their electrical bonding, and the disturbance leads to the phenomenon known as triboluminescence. If the crushing be carried out between two sheets of plate glass in a dark room, the crystals are seen to emit a soft violet luminescence as they are broken. At the Fritz Haber Institute in Berlin, Miss SCHÖNEWALD is measuring the electric charges liberated during this treatment of a number of different crystals. Interesting information may be expected regarding our fundamental knowledge of sucrose crystals from this angle.

In common with many other crystals sucrose crystals exhibit marked magnetic and electric phenomena; references are made in the bibliography to papers on these various studies. Of these the piezo-electric properties are perhaps the most interesting in connection with the crystallization of sucrose, since in the search for perfect piezo-electric crystals excellent papers have been published by several workers, notably Dr. SHEFTAL^{10, 12, 13}. Changes of temperature, or of pressure along the axis of certain crystals produce difference of electric charges between the two ends of the crystal. These are known as piezo-electric charges and such crystals are used exten-

sively for radio detectors in wireless work and for many allied purposes. For this purpose the crystal has to be as perfect as possible, and though sucrose could be so used, it has not been found so suitable as Rochelle salts, or as quartz. This is partly because it does not produce so marked a response, and partly because it is subject to serious intrusions and imper-



Fig. 1/43. ($\times 3,000$)

fections. So far, none have been able to determine the cause of, nor to eliminate such imperfections.

The internal structure of the sucrose crystal has not received a great



Fig. 1/44. ($\times 12,000$)

deal of attention hitherto. The differences met in the physical characteristics of different apparently pure crystals require fundamental studies on the causes of such variations. Knowing the causes of such variations, it may be possible to influence and to predict the form attained.

Remembering the remarkable electron micrographs which Dr. A. VAN-

HOOK had published at the 6th General Meeting of the American Beet Sugar Technologists in 1950, I felt that this technique might throw some light upon the distribution of the internal liquor in sucrose crystals and upon the consequent difference of structure between crystals having a high and low water content. VANHOOK had used alcohol-etched surfaces, but

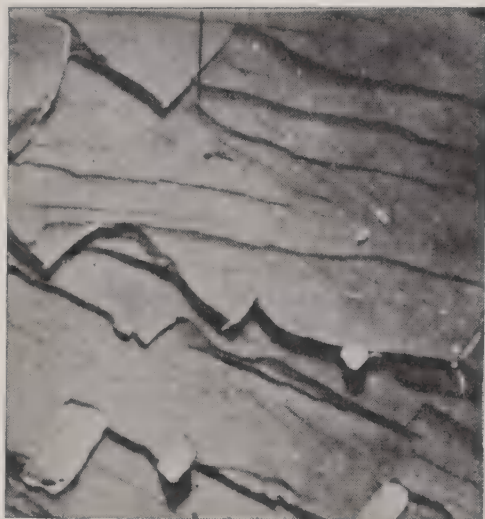


Fig. 1/45. ($\times 20,000$)



Fig. 1/46. ($\times 20,000$)

surfaces are frequently suspect for irregularities. We therefore used a cleavage technique and examined the internal surface thus exposed. This

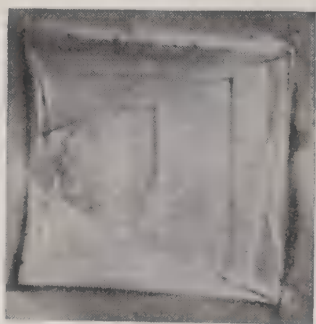


Fig. 1/47. Electron micrograph of one particle, resulting from finely grinding sucrose under alcohol ($\times 20,000$).

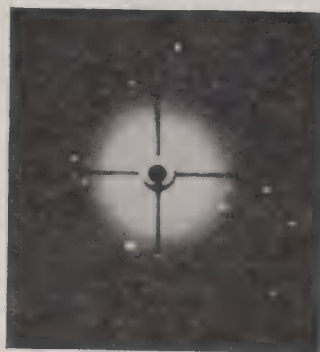


Fig. 1/48. X-ray photograph of sucrose crystal.

study was made in co-operation with the Associated Electrical Industries Research Laboratories, who prepared a series of micrographs and X-ray photographs of the two sets of provided sucrose crystals. Of the former, some showed a remarkable layering effect (Figs. 1/42 and 1/45) at 20,000 diameters magnification. This could not have been a conchoidal fracture such as

one may see in fractured glass; the edges were too sharp, and it could be assumed that this represented a definite internal structure. In Fig. 1/42 we can also observe features resembling moon craters. We do not yet know their significance, but we may suspect something real rather than a development of micrographic technique. Another micrograph (Fig. 1/44) reveals 'mosaic' structure. This confirms the observations of VANHOOK that it portrays an existing feature inside the crystal exposed by the cleavage plane parallel to the 100 face²¹. These micro crystal blocks or 'composite crystallites' are approximately a micron in length; they would exhibit internally a much more perfectly formed lattice structure than micrographs of whole crystals have revealed. We have no means of knowing what fills the interstices between these crystallites, it is an intriguing thought that this might be the site wherein non-sucrose, including water, may be located. MILES²⁵ advances this view in his study of the adsorption of gum arabic and dextrin into lead chloride crystals, and this view is also held in other fields.

Other micrographs show to a certain degree either layering or mosaic formation. The practical technologist will be interested to know whether



Fig. 1/49. Micro-photograph of layer growth on 100 face, repairing fracture on corner (60 $\times$).

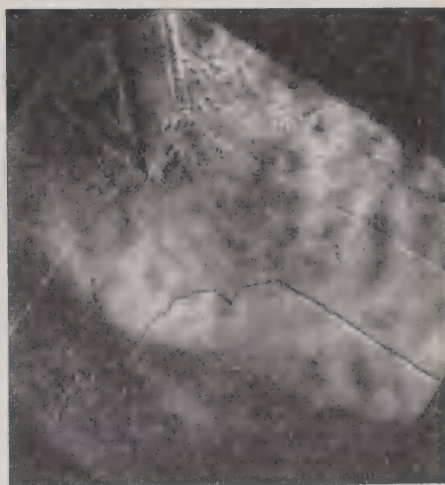


Fig. 1/50. Micro-photograph of layer growth, showing contrast in height of layers, also rectilinearity of wave front.

in crushing sugar the mosaic form will break the crystallites apart more readily than non-mosaic crystal. Several micrographs of sugar finely ground in alcohol indicate surviving crystallites.

With the evidence of layer formation in the sub-micron range of size, and the knowledge of the easy cleavage of the sucrose crystal, it seemed

possible that the growth of the crystal might proceed in some layerwise manner. A search of the literature failed to yield any evidence; Dr. C. W. BUNN of the Imperial Chemical Industries, who had reported upon the layer growth of various inorganic salts (Faraday Society Discussions 1949) had neither been able to observe layer growth with sucrose nor with various other organic non-polar substances. BUNN suggested that layer growth



Fig. 1/51. Micro-photograph of a complex pattern on the surface of a crystal of sucrose which had been immersed in solution for several months.

was characteristic only of polar or ionised substances. However, by observing clear sucrose crystals growing in a supersaturated liquor under the microscope, I was able to observe and to photograph the layer growth actually in progress; we have in 1956 commenced micro cinephotography thereof. At magnifications of 10 to 100 x, one may see a series of layers of varying height, some even visible by the unaided eye down to others barely visible under the highest magnification. Since the deposition of a certain number of molecules per square micron of surface will cause the extension of these layers inversely to their thickness, it is evident that the thinnest layers will spread most rapidly. These will continue to overtake and merge into the thicker layers and so progressively cover the crystal surface with an ever-changing and fascinating picture (Figs. 1/49–1/52). A damaged crystal will repair itself most rapidly²¹.

The author has reported that sucrose crystals can contain up to 1 % of liquor inside. Figs. 1/56–1/58 show some of the intriguing forms of this liquor

inclusion in pure sucrose crystals. Sometimes the pattern of the inclusions are suggestively symmetrical but incomplete, sometimes one can see no conceivable reason for so disordered a pattern of distribution. Sometimes the liquor-filled cavities are several tenths of an inch in length, yet again by using utmost magnification drifts of globules of liquor of still barely



Fig. 1/52. Micro-photograph of a complex pattern of layer growths.

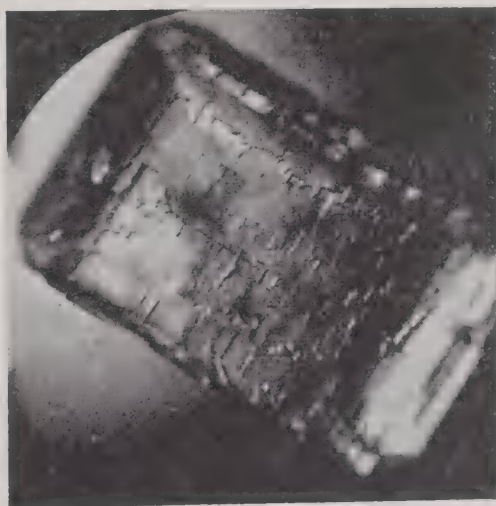


Fig. 1/53. Micro-photograph of crystal grown in agar gel, showing tessellated surface²¹.

perceptible size, probably of the order of a micron or less in diameter may be distinguished. It is possible that these explain the craters on Fig. 1/42.

Several photographs have been taken showing how the liquor droplets may be 'built into' the surface of the crystal by successive layers of crystal. A great deal of study has to be done before the mechanism of this phenomenon will be fully understood.

Allied to this is the investigation of the phenomena of inclusion of coloured nonsugars. Again such little information as is available is very



Fig. 1/54. Micro-photograph, showing surface tessellations on a crystal grown in agar gel²¹.

inadequate. Anyone who has examined numbers of raw sugar crystals under the microscope or coloured kandi crystals by the unaided eye will know that the colour distribution can be strikingly uneven (Figs. 1/59 and 1/60). Flecks of colour internally in raw sugar crystals may well be connected with insoluble suspended matter, but frequently one may see striking 'pattern distribution' of colour, either in drifts or groupings of grosser

* Since writing the above, the writer has obtained evidence that this is indeed the case, also that air may be included (B.S.C. Conference 1958, also *Nature*).



Fig. 1/55. Crystallisation of sucrose at very high supersaturations, reproduced by courtesy of Dr. BRIEGHEL-MÜLLER (290 $\times$).

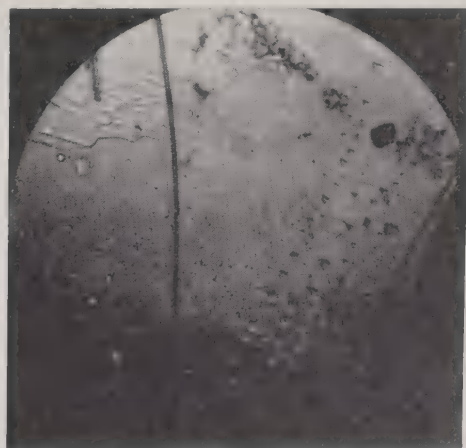


Fig. 1/56. Micro-photograph of layer growth, also fjord-like inclusions of liquor.
 Fig. 1/57. A most fortunate micro-photograph of layer growth, showing globules of liquor apparently just being overgrown.



Fig. 1/58. Micro-photograph of internal liquor very near surface, also surface outcrops.

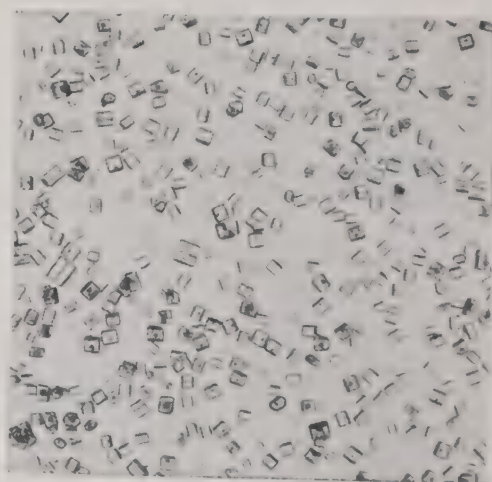
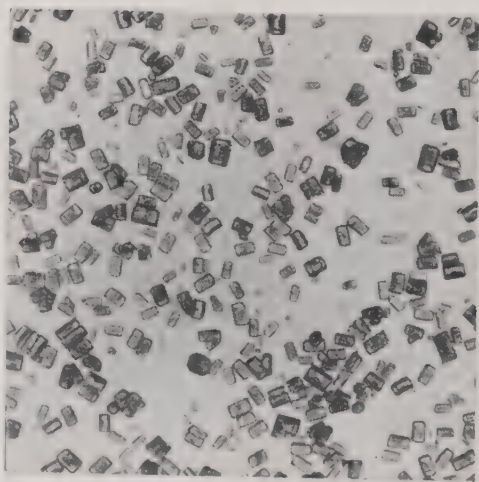


Fig. 1/59. Low grade boiling, showing the dark grain in the heart of the larger crystal.
Result of Einwurf boiling.

Fig. 1/60. Low grade boiling, showing an internal patch of dark colour not due to Einwurf boiling.



Fig. 1/61. Fine etching (40 $\times$).



Fig. 1/62. Deeper etching (40 $\times$).

liquor inclusions, or in patches of general colour which under higher magnification may be resolved into areas containing numbers of discreet inclusions. A kandi maker with generations of experiences behind him confessed that when a kandi tank was crystallising, he still was uncertain what colour and size the crystals would be, until they were actually taken out of the mother liquor and drained off.

Crystal faces are not dissolved uniformly all over the surface as might be expected. Not only does solution start at the projecting corners and edges, but in addition, small pits or angular cavities are produced. These are known as etch figures, and differ on the different faces, so much so, that faults in a crystal may be indicated by examining the pattern of the 'etch pits' and the 'vicinal' faces which bound the pits. They also conform to the particular symmetry class to which the crystal belongs. These rather remarkable etch designs may be produced and examined readily on large sucrose crystals by wiping with a moist cloth, or by immersing for varying time in nearly saturated solution, or even by exposing for a short time to air at over 90° relative humidity, then wiping with a dry cloth. (The Figs. 1/61 and 1/62 show a very lightly and a heavily etched surface, respectively.) Etching is produced by a surprisingly slight submission to unsaturated conditions.

7. Distribution of Impurities in Sucrose Crystals

Some excellent reports have been published on the structure and distribution of nonsucrose by PAINE and BALCH in 1926²², but many papers on this subject bear evidence of a confused picture, which is not surprising for such a complex phenomenon.

PAINE and BALCH showed by ultra filtration tests on beet sugar products that the colloidal nonsugars are distributed fairly uniformly throughout the crystal, but that in some cases grossly dispersed material was present at the centre of the crystals. Since the colloidal impurities in sugar are negatively charged (measured semi-quantitatively by the incremental addition of night blue to the sugar solution to be analysed whilst in an electric field, meantime watching the direction of movement by the particles under a microscope towards the anode or kathode) it could be assumed that the growing surface of sucrose crystals is slightly positively charged. So we can picture the grosser particles being associated with nucleation and the finely dispersed colloidal particles being drawn into the growing lattice. Certain dyes, notably certain caramels of a colloidal character²², which are negatively charged in solution, are bound continuously to the

crystal throughout its growth, which permits the production of the familiar coloured kandi. ALEXANDER reports that types of caramel exhibiting a pronounced negative charge are adsorbed more definitely than those having more positive charges. The author's findings indicate that soluble colouring matter is associated with liquid inclusions only, even superficially uniformly coloured areas resolving under high magnification into a dispersion of inclusions. Details are being given in a paper to the B.S.C. Conference 1958.

Regarding the inclusion of inorganic salts KEANE, AMBLER and BYALL²⁴, and others have reported that certain ions appear to be strongly adsorbed internally, as for example calcium and sulphite, whereas others, for example sodium and sulphate, are not.

Internal water. Whilst a wide range of nonsucrose components are known to be held within the sucrose crystal, probably that present in greatest quantity and having received least attention is *water*. This is not surprising, since for most purposes it is not objectionable and, moreover, it is not easily determined analytically. For various reasons this water structurally and physically merits careful study. It is interesting to speculate whether the reason for this water being bound in the growing lattice can be explained by or is related to similar electrical phenomena as is the syncrystallisation of colloidal nonsugars.

Our attention was attracted to the possibility of internal water by a dispute between the analytical laboratory, which found minimal water in large grained sugar, and some observant process men who were experimentally making this sugar into icing, who declared that the resulting icing appeared damp. At about the same time another observant process man sent up large crystals (M.A. 0.3"; see Fig. 1/35) every one of which exhibited perfect twinning. Assuming the possibility that if significant proportions of internal water will exist at all, it might exist in these crystals. A careful full analysis was made, with the challenging result that 0.23% remained unaccounted for! When the crystals were crushed before analysis a higher polarisation was obtained, due to drying during crushing. Applying vapour pressure measurement confirmed the finding in a most conclusive and satisfactory way. Refined sugar, as normally packed, shows an E.R.H. (Equivalent Relative Humidity)²⁰ of about 60, since the syrup on the external surface during granulation or drying crystallizes until the residual syrup is of low quality. The internally held syrup still retains its high quality, being that of relatively pure mother liquor, since its water cannot evaporate. When crushing such a sugar it exposes this syrup, which exhibits an E.R.H. nearer

that of pure saturated sucrose solution, *i.e.* 86. In the case of large kandi crystals there may be as much as 0.5% of internal water; the percentage drops off rapidly with decreasing M.A., so that normal granulated may be of the order of 0.03% or less. This phenomenon has been well known to those studying salt, but whilst some sugar chemists acknowledged that some water was occasionally present, few realised the extent of the intrusion. Whilst this internal water does not appreciably dry out, yet according to a suggestion by Prof. BERNAL it might respond to a temperature gradient across the crystal and migrate by solution and recrystallisation. A large kandi crystal so tested, showed an efflorescence of dried migrated syrup on the hot surface within several days. It is thus conceivable that it might contribute to concreting on long storage.

The distribution of nonsucrose other than water within the crystal is connected with the following processing conditions. Syrup, in quantity sufficient to keep the heating surface of the pan covered, is evaporated until supersaturated to a desired degree. It is then nucleated, either by the introduction of seed or by 'shocking', and, as the crystals grow, further syrup is fed into the pan until the pan is full and the grain has grown to the desired size. As PAINE and BALCH have indicated, the nuclei may well include coarser suspended matter, just as condensing moisture may include soot, etc. If the feeding syrup is of constant quality, the mother liquor tends to get richer in its nonsucrose constituents continuously until the crystallisation is completed. If, as is frequently the case, lower grade syrups are used for the feed, this progressive lowering of quality of mother liquor is rendered even steeper. It would seem a reasonable hypothesis to assume that each layer of sucrose crystallizing will take into its lattice 'absorbable' impurity in some degree proportional to the percentage present in the mother liquor at that stage. Thus the percentage of 'absorbable' (as distinct from suspended and colloidal) nonsugar content would increase from centre to surface of the crystal entering the centrifugal machine. Now comes a distinct increase in the gradient of impurity, as such syrup as may be left upon the crystal after centrifuging will by drying – particularly with granulated sugar – deposit a layer of rapidly worsening quality, thereby presenting its worst aspect to the eye of the observer! Finally, there will be a layer of exhausted syrup of low quality, and this is true even in the purest of granulated sugars. The dimensions of this layer can be estimated and it affects much of the physical phenomena which a crystal exhibits. A rough calculation suggests that the depth of the syrup layer on any crystal may be of the order of $\% \text{ ash} \times 120,000 \text{ \AA}$, neglecting the irregular distribution caused by the meniscus drawing the syrup to the points of contact. Thus,

for highly refined sugar with an ash of 0.003% then the syrup film will be 360 Å or about 36 molecules thick, taking 10 Å as a mean cross section. For a raw sugar it will be a hundred or more times as thick. Thus from a molecular point of view, the syrup layer surrounding a crystal is extremely important.

The above picture has to be modified for sugars produced by 'in boiling', in which small grained sugar is first produced by boiling from a low quality syrup, this being centrifuged, then returned as coarse seed grain to a higher quality pan, giving several cycles of impurity zoning.

8. Crystallographic Comments upon Cane Raw and Refined Sugars

(a) *Raw*

Since the London refineries receive raw sugars from practically every big sugar exporting area in the world, some could expect comment upon the



Fig. 1/63. Raw beet sugar, showing bad conglomeration.

general characteristics of sugars from various countries of origin. This is not quite so simple and to a certain extent it is impossible. Owing to variation of climatic and soil conditions, of locally favoured cane and beet varieties, and of processing technique at different factories in the same country, sugar from one country of origin may show even greater variation

than sugars from entirely different production centers. This is strikingly true regarding raw sugars from Queensland and from Hawaii, and it is doubtless true to a greater or lesser extent regarding sugar from most large areas (Fig. 1/63–1/65). The complexity of the general aspect of this subject may be illustrated by a few remarks. The ‘relative proportion’ of



Fig. 1/64. Raw cane sugar, showing reasonable uniform grain.



Fig. 1/65. Raw cane sugar, well formed but very mixed grain size.

various nonsucrose impurities is primarily a question of soil and conditions of cultivation, including cane varieties and use of fertilisers. Specific cane varieties under certain climatic conditions retain a significant amount of starch degradation products, and yield raw sugars giving filtration difficulties to refiners who use carbonatation, but less to those using kieselguhr filtration as one step in the purification of the raw liquors. The fact that this effect is relatively unaffected by the intensity of the washing or affination process suggests a considerable degree of absorption or inclusion of these colloidal nonsugars within the crystal. Evidence is now slowly coming to hand as to the nature of these impurities.

The extension of ‘inboiling’ technique makes the amount of nonsucrose retained in the heart grain greater, a feature which may be observed in some affined sugars, wherein the darker seed crystal is visible within a paler later growth (Fig. 1/59–1/60). Some raw sugar factories are characterised by

uniform well-shaped sugar crystals which any panman would be proud of, others very definitely never come into this category.

(b) *Refined*

We mentioned in the beginning of this paper that sucrose as a commercial product is produced in many forms (Fig. 1/66, 1/67, 1/68). Reference was made to the evolution of kandi crystals as made today from the early efforts to produce large crystals by slow crystallisation in order to drain off more readily the impure mother liquor. In course of time the sugar manufacturer has learned to produce crystals which would have seemed miraculous to the early producer. There is still a tendency with many sugar refiners and manufacturers to keep to themselves some more intimate techniques as developed by past generations, but in essence the production of kandi crystals depends upon a long crystallisation time, under static conditions, with the temperature changes under very careful control. Up to ten days of slow growth are necessary for these crystals, averaging from two to four centimeters in length. It is interesting that the effect of impurities from different origins is reflected in these large crystals, and that since their

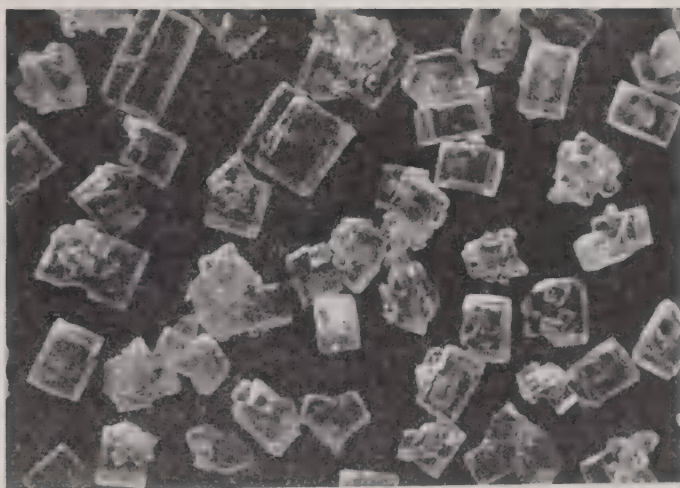


Fig. 1/66. A typical refined sugar, showing some clean grain and some bad conglomerates.

shape is so evident to the purchaser this might be unwelcome in many instances in what is so pre-eminently a traditional product. I have already referred to the deliberate production of coloured as well as colourless forms of kandi sugar.

From a historical origin point of view reference should next be made

to loaf sugar. This was one of the earliest ways in which small grained sugar was produced by the sugar refiner. The massecuite containing the large grains were run into conical moulds, stirred intermittently for a while, then allowed to continue the cooling process, causing the individual crystal to be cemented together by the further crystallisation. When the crystallisation

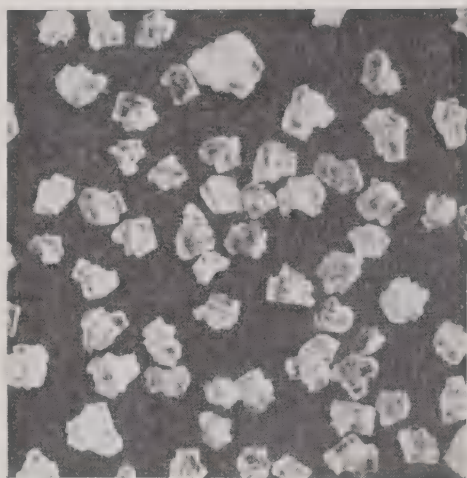


Fig. 1/67. Refined sugar X5, practically 100% conglomerates.

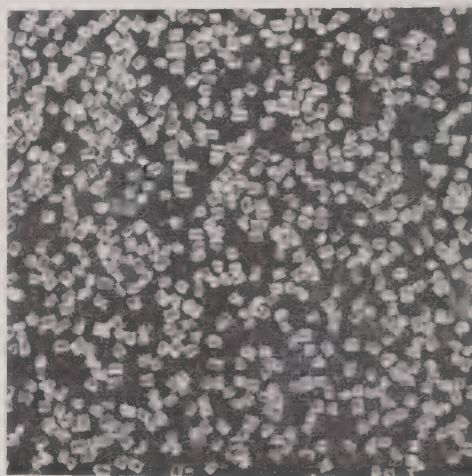


Fig. 1/68. Refined sugar. A good uniform grain with few conglomerates.

had proceeded far enough, plugs were withdrawn from the apex of the mould and the syrup was allowed to drain off. Liquoring syrup, made by dissolving earlier blocks to saturation, was then allowed to percolate through the entire cone, this slowly replacing the less pure mother syrup. Ultimately the conical loaf was dried. The whole process took several weeks from the dissolving of the raw sugar to the deliverable refined sugar. Lower quality cones were prepared similarly in much larger cones, producing coloured sugar which, when broken up, was sold to sweet makers and others as pieces.

When in course of time the old and slow cone process was speeded up by various means, the existing demand for these lower quality 'pieces' was met by the development and production of a lower purity small grained sugar, designed to retain the pleasantly flavoured nonsugars. Hence our present pieces sugar. From a crystallographic point of view, since the object in the case of pieces is to retain nonsugars, logically an aggregate grain would be the correct crystalline form. Those interested in the early development of these cane sugars should read the excellent account in *Sugar* by FAIRRIE*.

* G. FAIRRIE, *Sugar*, 1st Ed., Fairrie and Co., Ltd., Liverpool, 1925.

To revert to the production of loaf sugar, the old conical form is still produced in some parts of the world, but to avoid the long and tedious drainage period this is completed rapidly by using centrifugal machines. The cone moulds are placed in these to take advantage of the high gravity force in centrifugals.

The cutting of the cone shaped sugar block was not a very satisfactory process; a number of different processes were tried out, with the object of attaining a parallel sided slab, which would facilitate mechanical cutting into regular shaped pieces. Apart from the engineering involved, one might classify these processes into two groups according to the underlying principles. The first is virtually that of the old loaf process, in that the massecuite is poured from the pan into moulds and there allowed to cool over a lengthy period, during which the slow crystallisation from the mother liquor binds the crystals together most effectively. Probably the best example of this process is that known as the *Adant*, taking the name of its inventor, ADANT a foreman in a Belgium refinery in Antwerp. Devised in 1890, Thames refinery in London adopted it in 1894 and has used it successfully ever since.

The second group consists of those several processes wherein the massecuite is first spun in a normal basket centrifuge, as for granulated, then the moist sugar is pressed in moulds and the resulting blocks are dried in ovens.

The essential difference is the manner in which the cementing crystallisation is carried out. Great ingenuity has been displayed, and a great deal of research has been and still is being carried out, in order to attain the best results. The slow continuation of normal pan crystallisation, which forms the basis for the first group of processing, still offers the best way of attaining a richly sparkling sugar, better than the irregular drying characteristic of the second group. Nevertheless, one must admit that this is only attained by the use of an expensive plant and elaborate process.

Slab or porous forms of sugar may be and are produced for use in a variety of regular forms, as for example: cube, tabloid, slab and block, as well as roughly crushed or powdered sugar of various sizes. In all these the essential feature is that the crystals are presented in what may well be regarded as a porous form.

Still finer we have the pulverised or icing sugars, which may be produced by milling any form of sucrose, the individual crystals being broken down to the mean average size desired.

Fondant sugars are an entirely different presentation, in which the exceedingly small crystals of sucrose are surrounded by their own mother liquor. It is virtually a massecuite, generally at so high a grain content that

externally it appears an almost solid block, or, in the extreme form, a dry sugar. This grade is produced from high quality sugar liquors by evaporating high grade sugar liquors to a low water content, in some processes at high temperatures and after discharging from the concentrator, stirring violently. Extremely heavy nucleation takes place when the mother liquor is at a very high supersaturation. If the final form is required to retain plasticity – such as used by some confectioners – a small percentage of invert may be added before the final evaporation. This ensures an adequate proportion of uncrystallisable syrup remaining to preserve the desired malleability. The opposite extreme is that whereby a dry sugar is desired, and in this case evaporation is carried on at high temperature to a very low water content, before nucleation. The resulting crystallisation liberates so much heat that practically the whole of the water may be driven off during the crystallisation, and a reasonably dry lumpy or granular sugar results.

9. Particle Sizes of Granulated and Raw Sugars

The distribution of sizes of graining is one of the most important variables in refined sugar, and to a lesser extent in raw⁶². It is useless to attempt adequately to deal with the grist, as the distribution of the grain sizes* is commonly called, unless careful attention is paid (*a*) to obtaining representative samples by approved methods; (*b*) to the adequate accuracy of the sieves used; (*c*) to the operation of mechanical shakers for a period of time proven to be adequate for the type of sugar and the conditions of the test.

(*a*) Experience has demonstrated that one or more complete cross sections of the sugar output from a granulator or belt conveyor gives a representative sample. It is difficult to sample a pile of sugar satisfactorily owing to segregation of sizes. If a bag has to be sampled, or a sample for screen analysis has to be taken from a bag or tin, the best is to use a rotary or a 'flip flap' intermittent sampler, as is used for coal sampling.

(*b*) The discrimination possible in the light of the results of the M.A./C.V. method (M.A. = mean aperture, and C.V. = coefficient of variation for grist characteristics) is such that even standard sieves supplied by reputable makers may occasionally be found insufficiently accurate.

(*c*) It is desirable to carry out a series of gristings with time of screening as variable with any new apparatus, using typical sugar both of the coarse and the fine range. The finer the sugar and the higher the initial concen-

* In this text where the term grain size is used, this should be taken to indicate size as indicated by normal sieving methods.

tration per unit area of the sieves used, the longer the time necessary to ensure that the separation of the different grain fractions by sieving is reasonably complete. Sieves used should be of one of the recognised standard types for which true area of aperture is widely known, and for published results the type and series should be specified exactly.

There is no system of reporting the sizes characteristics of any particulate matter, which is so directly informative as adequate carefully conducted gristing, as above described. Nevertheless, it is difficult to form a mental picture of the appearance of a sugar from the extensive list of weight percentages of screen fractions so obtained.

10. Determination of M.A. and C.V.

The need for simple means of conveying the mental impression of sugar grain sizes is evident. Such a means would be, for example, to express the height and spread of the peak obtained by graphing '% on' against 'sieve aperture' on ordinary graph paper. PHILIP LYLE found that specimen series of sizes fitted into the requirements of a system we have since termed the M.A./C.V. system. The Mean Aperture/Coefficient of Variation system originated in the development in 1914 by HAZEN for plotting size frequency data⁶³. The validity of this method has been tested by careful gristing of many hundreds of Tate & Lyle refined sugars, and by examining many pu-

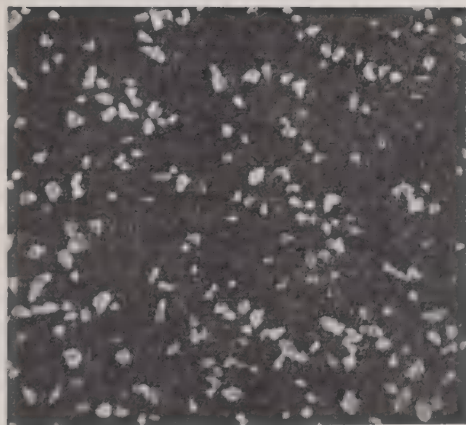


Fig. 1/69. Pulverised refined sugar X5.
M.A. 0.008; C.V. 22.

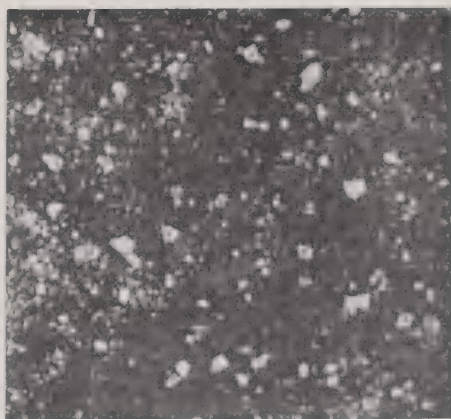


Fig. 1/70. Pulverised refined sugar X5.
M.A. 0.008; C.V. 56.

blished gristings. Normally occurring sugars do not depart from the requirements of the system, which are as follows. When the cumulative weight percentages are plotted upon arithmetic probability paper against sieve aperture as abscissa, the points must lie upon a straight line between 84.13

TABLE 4

T.L. GRAN (TABLE FOR 0.025 M.A.); INDICATION FOR M.A. GIVEN IN DECIMAL INCHES

Mesh 20 $\rightarrow$ $\frac{1}{35}$ on		3		4		5		10		15		20		25		30	
$\frac{1}{96}$ on	$\frac{1}{35}$ on	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.	M.A.	C.V.
68		0.0198	36	0.020	37	0.0202	38	0.0210	44								
70		0.020	35	0.0203	36	0.0205	38	0.0212	42								
72		0.0204	33	0.0206	35	0.0209	36	0.0218	40	0.0218	46						
74		0.0207	31	0.021	33	0.0212	34	0.022	39	0.0224	45						
76		0.021	30	0.0212	32	0.0214	33	0.0223	37	0.0229	43						
78		0.0213	28	0.0215	30	0.0218	31	0.0228	35	0.0231	41	0.0241	44				
79		0.0215	28	0.0218	29	0.022	30	0.023	34	0.0235	39	0.0244	42				
80		0.0216	28	0.022	29	0.0222	30	0.0231	33	0.0239	36	0.0247	40	0.0256	43		
81		0.0218	27	0.0221	28	0.0223	30	0.0233	33	0.0239	36	0.025	40	0.0259	41		
82		0.022	27	0.0223	28	0.0226	29	0.0234	32	0.0242	35	0.0251	38	0.026	40		
83		0.0222	26	0.0225	28	0.0227	29	0.0236	31	0.0245	33	0.0252	37	0.0262	39		
84		0.0224	25	0.0227	26	0.023	28	0.0239	30	0.0247	33	0.0256	34	0.0264	37	0.0273	39
85		0.0224	25	0.0227	26	0.0232	26	0.0242	28	0.0248	31	0.0257	33	0.0266	35	0.0275	38
86		0.0226	24	0.0229	25	0.0235	26	0.0242	28	0.025	31	0.0259	32	0.0268	34	0.0277	37
87				0.023	25	0.0238	25	0.0242	28	0.0251	30	0.026	32	0.0269	34	0.0278	35
88						0.0234	25	0.0243	28	0.0253	30	0.0262	31	0.027	33	0.028	34
89						0.0236	23	0.0247	26	0.0254	29	0.0264	30	0.0273	31	0.028	34
90						0.0238	23	0.0249	25	0.0257	28	0.0266	29	0.0274	30	0.0283	32
91						0.024	23	0.025	25	0.026	26	0.0267	28	0.0275	29	0.0285	31
92						0.0241	22	0.0252	24	0.026	26	0.027	27	0.0277	29	0.0285	30
93						0.0243	22	0.0253	24	0.0262	25	0.027	27	0.028	28	0.0288	29
94						0.0246	21	0.0255	23	0.0263	25	0.0272	26	0.0283	27	0.0289	28
95						0.0248	20	0.0258	21	0.0266	23	0.0272	25	0.0285	26	0.029	27
96						0.025	20	0.026	21	0.0268	23	0.0276	24	0.0287	26	0.0292	25

and 15.87%. If this is the case, the Mean Aperture (M.A.) is given by the aperture corresponding to 50% on this graph, and the Coefficient of Variation (C.V.) is given by 100 [aperture corresponding to 15.87% (or 16% approx.) minus aperture corresponding to 84.13% (or 84% approx.)] divided by 2 M.A., or $C.V. = \frac{\text{apert. for 15.87\%} - \text{apert. for 84.13\%}}{2 \text{ M.A.}} 100$.

Samples may be created by special riddling or mixing which do not obey this sample rule, exhibiting freak distributions. Accumulation of evidence has increased our original idea that the system is generally applicable, and is simple for comprehension and utilisation by men not trained in the field of science or mathematics, as pansmen, foremen, buyers and sellers of refined sugar, so that it is justified on its merits⁶⁵.

If the system be found satisfactory for specific types of sugar under

TABLE 5
SURFACE AREAS IN M²/KG; INDICATION FOR M.A. GIVEN IN DECIMAL INCHES

M.A./ C.V.	15	20	25	30	35	40	45
0.005	34.4	34.7	35.3	36.3	37.0	38.1	39.5
0.010	17.2	17.4	17.7	18.2	18.5	19.1	19.7
0.015	11.5	11.6	11.8	12.1	12.3	12.7	13.2
0.020	8.6	8.7	8.8	9.1	9.3	9.5	9.9
0.025	6.9	6.9	7.1	7.3	7.4	7.6	7.9
0.030	5.7	5.8	5.9	6.1	6.2	6.4	6.6
0.035	4.9	5.0	5.0	5.2	5.3	5.5	5.6
0.040	4.3	4.3	4.4	4.5	4.6	4.8	4.9
0.045	3.8	3.9	3.9	4.0	4.1	4.2	4.4

Compiled from:
1. M.A. = 50% (*R*₂) on mesh size *X*₂
 $C.V. = \frac{X_1 - X_2}{X_2} 100$ where
*X*₂ = mesh size for 16% (*R*₁)
2. Exponential equation in HONIG, *Determination of the Cryst. of Sugars*.

TABLE 6
APPROXIMATE NUMBER OF SEPARATE GRAINS x10⁷ PER KG AT VARIOUS M.A. AND C.V.'S;
INDICATION FOR M.A. GIVEN IN DECIMAL INCHES

M.A./ C.V.	25	35	45
0.005"	227	323	488
0.010"	15	65	139
0.020"	2	20	70
0.030"	1	11	57
0.040"	0.5	11	52

Assumptions:
1. Crystals are spheres of diameter midway between mesh sizes shown on graphs;
2. Crystals on 10 mesh have diameter midway between meshes 8 and 10;
3. Crystals through 200 mesh have diameter half that mesh;
4. Sugar sp. gr. = 1.585.

consideration, a simplification is evident *i.e.* that instead of using a number of sieves, two suitably chosen sieves will give the desired line. We have calculated a series of tables from which the M.A. and C.V. may be rapidly obtained. (Table 4)

HONIG has stated frequently that for the technology of sugar manufacture

[crystallisation, centrifugation, drying and storage (caking)] and for the keeping quality of sugar the surface area of sugars is of considerable interest. A reference table (Table 5) is given, representing approximate surface area for sugars of the indicated sizes. A great practical importance may be attached to the number of contact points between adjacent crystals, since

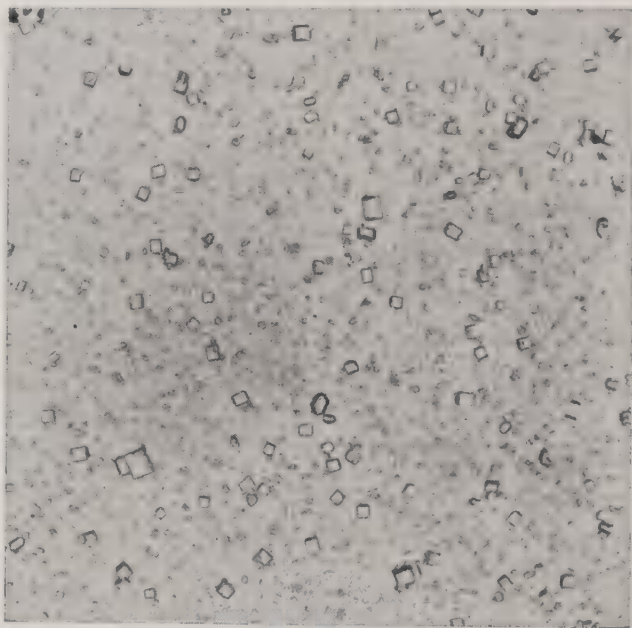


Fig. 1/71. Low grade boiling. Grain so mixed that it virtually will not spin.

syrup is held in processing here by capillary attraction. In Table 6 the approximate number of crystals is given as an indication of the frequency of the number of contact points. The number of crystals mounts up with decreasing size to a greater extent than the surface area does.

In the determination of the grain size of sugars and in the reporting of the results of screen analyses of granulated sugars it is customary in a number of sugar producing areas to use English units and in other countries the metric system is used. The designation of screens is usually given as the number of openings per linear inch. The following screens, with the corresponding openings in inches and mm, are used in the analyses of sugars (Table 7).

Other systems of size specification

The desirability for a uniform system to report the average grain size and its uniformity has been recognized for a long time*. Dr. BRIEGHEL-MULLER

* The need for conveying the mental impression of sugar grain sizes had led to several suggested presentations (see: *Arch. Suikerind. Ned.-Indië*, 36 (1928) 641).

TABLE 7

Tyler sieves	10	12	14	16	20	28	32	35	48	100	150	200	270	325
Corresp. U.S. B.S. sieves	12	14	16	18	20	30	35	40	50	100	140	200	270	325
Opening (inches)	0.065	0.055	0.046	0.0390	0.0328	0.0232	0.0195	0.0164	0.0116	0.0058	0.0041	0.0029	0.0021	0.0017
Opening (mm)	1.651	1.397	1.168	0.991	0.833	0.589	0.495	0.417	0.295	0.147	0.104	0.074	0.053	0.043

of the Danish Sugar Co. brought forward at the 1934 ICUMSA meeting, at which the above M.A./C.V. method was presented by POWERS, a similar suggestion, in which logarithmic scale for the abscissa, giving the grain size or screen aperture instead of arithmetic scale was used. Other technologists were thinking upon similar lines. BENNETT⁶⁴ in England, working

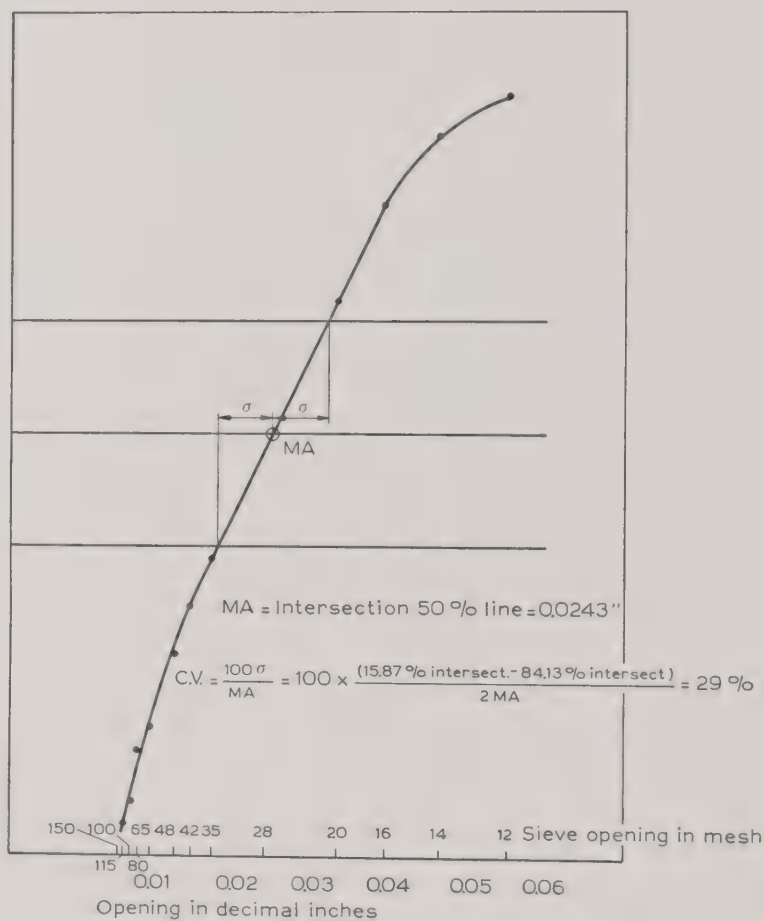


Fig. 1/72. Graph, illustrating M.A. C.V. technique.
M.A. = intersection 50% = 0.0243".
C.V. = $100 \times \frac{(15.87 \% \text{ intersect.} - 84.13 \% \text{ intersect.})}{2 \text{ M.A.}} = 29 \%$.

upon coal and later ROSIN, RAMMLER and SPERLING in Germany developed a useful system for the grading and expressing uniformity of pulverized materials. For the sugar industry a method was developed by the Süd-deutsche Zucker A.G., specifically suitable for application to sugar problems. A method similar to the latter was put forward at the ICUMSA meeting in Paris in 1954 by HONIG.

ROSIN, RAMMLER and SPERLING found that the size distribution curve for disorderly dispersed materials can be represented by:

$$R = 100 e^{\left(\frac{-d_1}{d}\right)}$$

where

R = screen residue

d = screen opening in mm.

BENNETT found that when $R = \frac{100}{e} = \text{ca. } 36.8\% = \text{average grain size.}$

By considering two screen openings d_1 and d_2 with residue R_1 and R_2 and using double logarithms for the ordinate, giving the accumulative screen residue R and a logarithmic scale for the abscissa, being the screen opening d the average grain size d and n the distribution of screen fractions for the average grain size d can be found in a simple way.

At the 1954 ICUMSA meeting the M.A./C.V. method was recommended for use with refined sugars; further investigations were recommended of the relative merits of the several recommended and published methods.

Regarding the practical significance of grist and form HONIG⁶⁴ has stressed in a number of papers the importance of grain size and uniformity as important in pan boiling, centrifugal separation, drying, etc. It is helpful to be able to compute the surface area and the number of crystals of unit of weight as an indication of the number of points of contact, tending to hold excess syrup by surface tension effect. It must be realised that other significant factors may be superimposed; if too simple a conception is adopted for a complex problem, incorrect inferences are inevitable. In this connection we refer to the contrast between conglomerates and regular crystals. Practical experience has simply demonstrated that sugars with a high C.V. will not spin as well as one of low C.V., owing to closer packing and decreasing porosity. Very fine dust or false grain of the order of 1/25 of the M.A. is partly thrown off with the syrup and partly retained in the residual layer of syrup surrounding the larger grains. The surface of crystals is far from planar, making it an approximation to compute the effective surface area. A practical test by spinning off a synthetic magma under standard conditions is probably the most informative in the holding capacity of a certain grade of sugar crystals.

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General nature of growth and form of sucrose crystals

- ¹ WOLF, *J. prakt. Chem.* (1843) 28, 129.

Crystalline forms, system, ratio of axis, etc.

- ² P. WULFF, *Z. Ver. deut. Zuckerind.* 35 (1885) 899; 37 (1887) 917; 38 (1888) 226, 1076.

- ³ P. GROTH, *Chemische Krystallographie*, Vol. 3 (Sucrose), 1910, p. 448.

Crystal class is mono-clinic sphenoidal *i.e.* twofold axis. Axial ratios and angles are given, also indices and calculated angles as obtained by various workers – showing considerable diversity. Cleavage distinct on (100). Speed of solution greater on 010 than on 010, etch figures with water are asymmetric triangles on 110 with one edge parallel to C, on (110) they are rhomboids with long side parallel to edge P'C and short edge to C.

Reported double refraction and refractive index data, dispersion and rotation, latter being -22° for light down the optic axis almost perpendicular to 100 and $+64^\circ$ per cm for the other.

He also gives a note about the electric polarisation.

- ⁴ J. A. KUCHARENKO, *Planter Sugar Mfr.* 80 (1928) No. 19, p. 382, 424.

Reports sp. gr. of 106 crystals of weights varying from 0.5 g to 1455 g. The sp. gr. varied from 1.5777 to 1.5889, mean 1.58495. Suggested that variations due to conditions of crystallisation and to small inserted air bubbles. KUCHARENKO measured surface area of each face on ten large crystals and calculated $\frac{S}{p^2}$ where S = surface area in mm^2 and p weight in g. This varies from 4.2315 to 3.987, mean 4.1227, showing 18 faces in all.

Two measurements given:

Wt	a	r	p	c	o	q	r^1	p^1	a_2
2511	11988	5338	5222	7105	503	2148	1081	3089	9422
1388	7477	4448	5004	2639	81	949	418	3695	6964

Wt	r_2	p_2	c_2	o_2	q_2	r_2^1	p_2^1	o_2^1	o^1
2511	5197	2089	8122	398	1112	812	6587	—	—
1388	5057	4252	4594	—	508	100	4760	—	—

- ⁵ F. P. PHELPS, *Intern. Soc. Sugar Cane Technologists, 4th Congr.*, 1932, Bull. 104.

Discourse upon geometrical theory of crystal structure. For solids bounded by solid surfaces and fulfilling the law of rational indices, there are 32 types of symmetry possible. BRAVAIS found 14 possible space lattices and SOKUKA 65 point systems, the latter being two or more interpenetrating space lattices. Enantiomorphous similarity with the various modes of combining the two forms adds another 165 possibilities making a total of 230 types. Sucrose belongs to the monoclinic system class 4; it is shown how this is determined; the author describes the use of the Goldschmidt goniometer for, measuring the angles, the representation on paper, and the definition and use of Miller's indices.

PHELPS stresses the lack of perfection of faces leading to variation of angles reported

* Under this heading are included not only references from the text but also other literature deemed of interest.

by various workers and gives extensive figures as reported. The variation in refractive index of the sucrose crystal is discussed, also the different optical rotation. Finally P. discusses the effect of impurities on the form and relative development of faces. A classical report on crystallography of sucrose.

Also see summary in C440 of the U.S.N.B.S.

- ⁶ K. ŠANDERA, *Z. Zuckerind. Čechoslov. Rep.* 57 (1932) No. 41, p. 333.

Observations upon the form of crystals grown between two plates under various conditions and in presence of various nonsugars.

- ⁷ G. VAVRINECZ, *Magyar Chem. Folyóirat* 42 (1936) 124; 43 (1937) 176.

Observations, measurements and diagrams of the numerous forms occurring in syrup and juices in the refinery.

- ⁸ G. VAVRINECZ, *Intern. Sugar J.* 41 (1939) 29, 345.

An original study on crystal forms of sucrose. 14 different forms are confirmed, a further 7 yet to be confirmed. Excellent illustrations of different forms, including a triangular form from Java syrup with a high invert content.

- ⁹ G. VAVRINECZ, *Deut. Zuckerind.* 66 (1941) 683, 728, 739, 753, 775, 788, 801 and 834.

A summary of present knowledge of sucrose crystal morphology with numerous tables, photographs and sketches. A valuable contribution.

- ¹⁰ N. N. SHEFTAL, *Compt. rend. acad. sci. U.R.S.S.* 31 (1941) No. 1.

SHEFTAL, a geologist, was seeking a perfect crystal for piezo-electric work. S. grew a number of large crystals under exact temperature control from 1.084–5 to 1.092–3 Supersat.

Found simplest form produced at lower supersaturations, number of facets increasing with supersaturation. Simplest form only a (100), c (001), p (110) and p' (110), also most homogeneous. S. suggests that at high supersat. crystal again tends towards simplest form.

- ¹¹ C. A. BEEVERS and W. COCHRAN, *Nature* 157 (1946) 872.

Classic X-ray examination of sucrose. Patterson-Harker direct method was unsuccessful, so used isomorphous $C_{12}H_{22}O_{11} \cdot NaBr \cdot 2H_2O$ (and chloride) by Patterson and Fourier methods. Full measurements are given and the construction shown to be 1 glucopyranose – 2 β fructofuranose (Fig. 1/73).

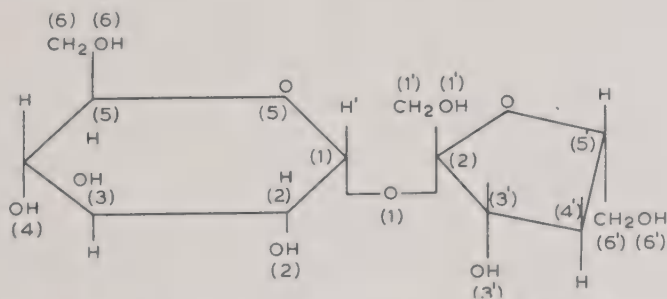


Fig. 1/73. Diagram of sucrose molecule after Dr. BEEVERS.

- ¹² N. N. SHEFTAL, *Trudy Inst. Krist. Akad. Nauk, S.S.S.R.* 3 (1947) 71.

Reports fibres and wire can be overgrown without causing cracks, but changes in temperature cause cracks which may be perpetuated or sealed off according to conditions of growth. Reports stratification lines, also liquor filled constructions which S. suspects may be connected in some way with the lines. Puts forward a picture of

mechanism on molecular kinetic theory. Reports sub-individuals of varying size found in descending frequency on 001, 100 and 110 and rarely on 110. Also reports growth pits, vicinals, etc.

- ¹³ N. N. SHEFTAL, *Inst. Cryst. Acad. Sc. U.S.S.R.* (1948).

Practical details of procedure reported in refs. ¹⁰ and ¹². Temperature control to 0.05°C still and 0.0015°C when stirred. Temperature 49°C.

- ¹⁴ BELVAL, *Sucr. belge* 68 (1948) 68, 194.

Review of molecular structure of sucrose.

- ¹⁵ YOUNG, *J. Phys. & Colloid Chem.* 53 (1949) 1334.

Report upon hemipenta- and hemiheptahydrates of sucrose with m.p., solubility, X-ray diffraction, optical and crystallographic data.

- ¹⁶ G. VAVRINECZ, *Mezőgazdasági Ipar* 4 (1950) 21.

A dissertation upon crystal forms, particular detail on twinning. Ratio of lengths on *c*- and *b*-axis defined as 'slenderness'. Full description of 20 samples from Canada, Holland and Hungary, including some from maple and sorghum.

- ¹⁷ *La Crystallisation du Sucre*, being a full report of the C.I.T.S. meeting in Brussels 1953.

Much inspiration may be derived from reading and rereading this report. *Sucrierie belge* 74 (1955) 263, 325.

- ¹⁸ P. HONIG, Treatises on microscopic examining of sugar crystals, *Arch. Suikerind. Ned. en Ned.-Indië* 35 (1927) 693.

In the period between the two world wars, many of us rated the Dutch team in Java as virtually the leading experimental sugar technologists of the world. Some outstanding papers were published by members of this team on the crystallization process, notably those by THIEME in 1928 *Studies in Sugar Boiling*. Unfortunately, publication of much of their work was restricted after 1932, as a part of a new policy set by the Board of the Java Experimental Station, thus denying the Java technologists the satisfaction of maintaining their high reputation, and the rest of the sugar world the undoubted stimulation thereof. Only some of these reports are now available; I owe to Dr. HONIG the receipt of a copy of his work and of his collaborators upon crystal studies, from which I have drawn a number of observations which reflect great credit upon Dr. HONIG and his team.

When false grain has formed during the boiling of a pan of sugar, it is the custom to dissolve such by additions of water, or light juice. This not only dissolves the unwanted grain, but also corrodes and etches the larger crystals. Contrary to the general belief (quoting HONIG), further crystallisation does not readily set this right, hence the solution should never be allowed to become unsaturated. Dissolving action takes place along the axes of symmetry of the crystal, and stresses are set up inside the crystal, probably by the local endothermic solution, leading even to splitting on rupture. Needless to say this emphasises the undesirability of slovenly use of water in pan boiling, also of either steam or water use in centrifugals, since these recessions will hold mother liquor. Liquoring in the centrifuge is here presented as preferable to steam or water washing from the point of view of crystal form.

Reference is also made to the deleterious effect of graining upon a turbid solution, whereby nuclei form upon and include particles of foreign matter, and an intriguing observation is that sometimes strikes become opalescent just before grains are formed, this clearing as the grains grow to visible size. HONIG's suggestion is that this must be due to the turbidity being absorbed by the growing crystals. My own view is that this may be connected with differential growth rates, at sub-micron size. The

observation is made, that ultramarine is not held within the crystal. There are some interesting micro-photographs illustrating the text, but unfortunately these would not lend themselves to good reproduction.

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(2) calculation from tensile strength (150 ergs/cm²);

(3) computation from the surface tension of the liquid (given by QUINCKE as 66.9 dynes/cm);

(4) empirical calculations from compressibility, coefficient of expansion, density and m.p. (360, 170, 80 and 20 ergs/cm²);

(5) applying pastes of varying surface tension to the solid and judging the values equal by complete wetting (230–250 dynes/cm);

(6) calculation from the heat of solution of fine crystals (5 ergs/cm²);

(7) calculation from the enhanced solubility of fine crystals (20 ergs/cm²);

(8) calculation from the hardness (370 ergs/cm²). The unweighed average is 224 ergs/cm² for the solid surface tension, 84 ergs/cm² for the interfacial tension. The difference (140 ergs/cm²) is at least within the range of surface tension of saturated solutions (80 ergs/cm²) in accord with YOUNG's condition with complete wetting of the solid by its mother liquor.

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CHAPTER 2

THE SOLUBILITY OF SUCROSE IN IMPURE SOLUTIONS

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1. Introduction

The solubility of sucrose is a subject of considerable importance when carrying out the process of crystallisation whether by boiling or cooling. As an important physical property of sucrose it has already been considered briefly by HIRSCHMÜLLER¹. The solvent of greatest interest is water which in the first place is the natural medium containing the sugar in solution in the plant cells, and to this is added further quantities of water used to aid the processes of sucrose extraction.

Sucrose is generally thought of as being very soluble in water, and this is true when considered on a weight basis as one gram of water will dissolve 2.19 g of sucrose at 30° C, whereas it will dissolve only 0.36 g of sodium chloride or 0.37 g of potassium chloride. In fact it compares with such soluble electrolytes as ammonium nitrate at 2.4 g per g of water. Among organic solutes of related chemical type its solubility lies between that of glucose at 1.2 g and that of fructose at 4.4 g per g of water.

It is also of interest to consider the solubility in relation to the number of molecules dissolved in a unit quantity of water, as this gives a more realistic picture of the concentration of entities in the solvent material. For this purpose the *molal* concentration is a quantity sometimes used for comparison as it is also useful in physico-chemical considerations of properties related to solution concentration. The molal concentration represents the number of gmols of solute contained in 1000 g of solvent, which for the time being is water.

Thus a solution of sucrose in water at 30° C has a molality of 6.4 when saturated; which is of the same order as 6.7 for glucose and 6.2 for sodium chloride, whereas potassium chloride is a little lower at 4.95 *M*, and both fructose and ammonium nitrate are very much higher at 24.6 *M* and 30.2 *M*

respectively. Although with the ionic solutes there may be more numerous entities at dilute concentrations when ionisation is more or less complete, the values indicated for saturating conditions are as representative as we are able to suggest as little is known of the degree of ionisation of saturated solution under such conditions.

If we go a stage further and consider also the solvent on the basis of molecular entities we see that one molecule of sucrose requires 8.7 molecules of water as solvent at 30° C and this rises to 10.6 at 0° C and falls to a value of the order of 3.9 at 100° C.

2. Solubility Determination

The determination of the solubility of sucrose is more difficult to carry out with a high degree of precision than is the case for most inorganic solutes. The main difficulty lies in correctly ascertaining that the solution is truly in equilibrium with the solid phase. This is particularly so at low temperatures when dealing with pure solutions. Other solutes present with sucrose and which increase the viscosity of the solution are generally believed to make the determination more difficult. This may not always be strictly correct if the views of VAN HOOK² are accepted concerning the influence or otherwise of the viscosity on rate of crystallisation. VAN HOOK considers that viscosity is not the factor primarily controlling the rate of crystallisation, in which case when equilibrium is being approached from a supersaturated solution the factors influencing the ease of approaching equilibrium would be those which influence the rate of crystallisation. On the other hand when equilibrium is being approached from the undersaturated region the influencing factors will be those which influence rate of solution. Rate of solution is not necessarily the same as rate of crystallisation and is generally more definitely rate controlled by viscosity and convection influences.

The simplest method for carrying out solubility measurements and the one which is preferred by KELLY³ is to prepare synthetically the required mixture from weighed quantities of solute(s) and solvent with sufficient of the saturating solute to provide about 20% by weight over and above that required to saturate the solution. A total of 20 g of synthetic mixture is a suitable quantity to weigh into tubes, tightly stopper and clamp to a framework to be rotated in a constant temperature water-bath. Using tubes 6" × ½" it has been found that 4 r.p.m. is a satisfactory speed at which to rotate the rack. This procedure turns the tubes end-for-end with a frequency which is suited to viscous solutions. With very viscous solutions agitation may be improved by including one or two short glass rods in each tube.

A period of 14 days has been preferred by KELLY for this technique but it is likely that a shorter period would suffice. WISE and NICHOLSON⁴ examined the time required to reach equilibrium in the case of pure solutions of sucrose from the point of view of rate of crystallisation data. They indicated that the time taken for a sucrose solution having a saturation coefficient of 1.02 to reach a value of 1.002 (*i.e.* as close to equilibrium value as can be experimentally distinguished), when placed in contact with crystals of surface area 0.05 m² per 100 g of water present, is 30 days at 0° C, 3 days at 20° C and 9 h at 50° C. These times were calculated for unstirred solutions and they considered that stirring could well reduce the times by about six-fold. Generally tests conducted to approach equilibrium from the undersaturated region were preferred, but some tests which have been conducted with the approach from the oversaturated region have shown no significant influence on the results in most cases. At the end of the agitation period the tubes may be removed from the rack and allowed to stand in the bath in a vertical position until suspended solids have settled. Generally not more than 24 hours has been found necessary for this procedure, although pressure filtration has been used occasionally in some of the really viscous systems which have been examined and in which suspended crystals show no tendency to settle even in 7 to 14 days. It is an advantage to use crystals of 0.8 to 1 mm in size (+20–16 mesh Tyler screen size) from which the small crystals have been removed by sieving.

For the preparation of phase equilibrium diagrams (*q.v.*) when original mixtures have been prepared from weighed ingredients, it is necessary only to analyse the clear liquid. This can be transferred from the top of the tube to a stoppered weighing bottle by means of a suitably warmed pipette. This technique is essentially that recommended by HILL and RICCI⁵ to which they apply the term 'synthetic complex method' and has been found by KELLY to be more suitable for systems with viscous solutions than the SCHREINEMAKER 'residue method'. The latter requires suspended crystals to settle into a compact mass and the analysis of this compact mixture is contrasted with the analysis of the clear supernatant layer. Owing to the very viscous nature of many of the solutions containing sucrose and other solutes the physical difficulties in obtaining a reasonably concentrated 'residue' may be substantial.

A method resembling that used by KELLY was used by KALSHOVEN⁶ and later by THIEME⁷ to determine the solubility of sucrose in naturally occurring molasses samples. When examining samples of molasses it is generally redundant to weigh out initial quantities of sucrose and molasses before mixing.

Whilst this method appears to provide reasonably satisfactory results it suffers from the disadvantage of taking a long time to perform. However, if there is no urgency to obtain the data, this disadvantage is not as serious as may first be thought to be the case. It is possible to operate with 30 or more tubes on a single rack, and by arranging the schedule so that three new tubes are clipped into position each day, an 'assembly line' type of procedure may be adopted to provide a regular supply of data. There are, however, circumstances in which a rapid determination is more advantageous especially for samples of molasses in association with factory operation.

In Australia a method has been developed by HARMAN⁸ who employed microscopic examination of a sugar crystal in a sample of molasses. The original 'saturation cell' was made of glass, and water of a suitable temperature was circulated through the cell block. This has more recently been supplanted by electrically heated microscope substage equipment with a glass thermometer or thermocouple head suitably embedded in the massive metal block. These cells are preferably of copper construction providing maximum opportunity for conductance of heat. A feature which is important for accurate results is to be able to control effectively the rate of temperature rise. Electrically heated cells⁹ are much more amenable to this than water-jacketed cells. A continuously variable transformer has been found to be the most effective piece of equipment to aid temperature control. Experience has indicated that temperature readings with these units should be checked against the m.p. of several pure substances over the temperature range of interest.

The technique involves placing a drop of molasses on a microscope cover glass, introducing a milligram or so of finely powdered sugar, preferably chip shaped particles, and covering with a thin cover-glass. The temperature at this stage should be lower than the saturation temperature of the sample, *i.e.* it should be supersaturated. It is necessary to observe the precaution to seal the edge of the cover glass by exuding a little molasses. Cotton wool padding placed around the objective of the microscope to cover the exposed top of the glass circle reduces the loss of heat to a minimum. In some types of micro-melting point sub-stages an air chamber under a flat glass disc provides thermal protection and the objective of the microscope is focussed through the glass disc as well as the top cover glass.

A magnification of 200 diameters has been found to be the most satisfactory. The edge of a chip or crystal is observed as the temperature is raised. The temperature at which erosion of the edge is seen to commence is noted as the saturation temperature of the sample *i.e.* the temperature at which it is saturated with respect to sucrose. Generally two observations

should be made, the first in the nature of a trial with heating at the rate of about 1°C per minute. This may result in a temperature about 3°C too high being noted. A second sample should then be taken and heated to within 5°C of the approximate saturation temperature before adding the sucrose crystal. A rate of heating of $\frac{1}{3}^{\circ}\text{C}/\text{minute}$ should enable the saturation temperature to be observed with a satisfactory degree of accuracy.

Intermittent testing is liable to give erroneous results and the change of crystal outline is more accurately related to temperature with continuous heating.

The eye has a tendency to tire after a period of intense observation while waiting for the edge of the crystal to start dissolving, particularly if a large number of determinations is being made. It has been found advantageous to employ polarised light in addition to ordinary light and to work alternately between these two conditions. The eye is thus rested somewhat by providing a changed distribution of colour in the field. Too rapid alternation will also induce eye-fatigue.

If extensive work of this character is being carried out it is recommended that the observer should check his technique not only for accurate temperature recording with the aid of melting point determinations with pure substances, but also with solutions of known saturation temperature established by the previously described technique of agitated suspensions of crystal.

The saturascope technique as just described is *not recommended* for syrups having a purity greater than 60%. It is generally suitable for the more viscous and lower purity materials experienced with final molasses when rates of crystallisation are slow, but should be considered with the maximum of caution and with adequate standardisation of technique if any attempt is made to apply it to syrups of purity higher than about 60%. Also it is not recommended for synthetic solutions, except under special circumstances when conditions simulate those experienced with naturally occurring final molasses.

A warning is given when interpreting results of saturation temperatures of molasses which may be measured in this manner. The implication exists that the molasses is supersaturated with respect to sucrose at temperatures below the value at which dissolving of sugar is observed. This does not necessarily mean that sucrose will crystallise within reasonable time under these so-called conditions of supersaturation¹⁰. If such information is desired it can be obtained only by carrying out actual crystallisation tests.

MILLICENT TAYLOR¹¹ used a refined modification of the saturascope technique to determine the solubility of sucrose over the temperature range

64–80° C. She employed a rather elaborate glass cell contained in the well of a temperature controlled water-bath. Temperature was measured with carefully calibrated thermocouples. The seeding crystals were at least two in number and 0.5–0.25 mm in size. Exceptionally painstaking precautions were adopted with the object of obtaining the maximum attainable accuracy. For example the rate of temperature change was generally less than 0.02° C/min and the calculated probable error of temperature observation was $\pm 0.053^\circ \text{C}$ in the sense that chances that the error is greater or less than the true value are even.

A method requiring as many refinements as employed by MILLICENT TAYLOR is not likely to find favour among workers outside of academic institutions or for applications other than for pure substances for which data of the highest degree of accuracy is of fundamental importance.

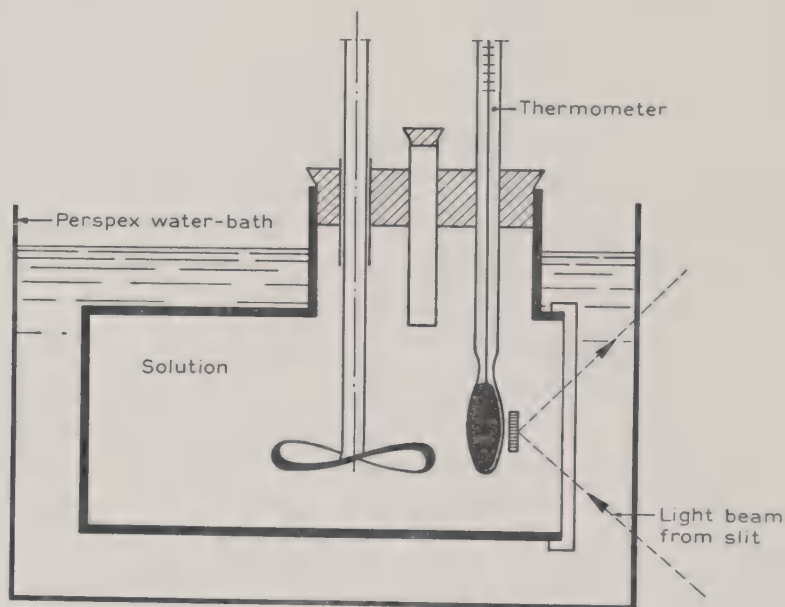


Fig. 2/1. Apparatus similar to unit used by WISE and NICHOLSON for measuring saturation temperatures.

Recently WISE and NICHOLSON¹² used for sugar solutions the method first described by DAUNCEY and STILL¹³ (Fig. 2/2). In this method a beam of light reflected from the surface of a crystal in the solution under examination is observed and a clearly defined change in the angle of reflection is associated with the saturation temperature.

The solubility cell initially described by WISE and NICHOLSON employed a two-inch T-piece pipe fitting which was machined smooth and silver plated (Fig. 2/1). This had a capacity of approximately 100 ml. Perspex

discs were fitted to the ends with a rubber gasket, and the short upright arm of the T-piece carried a rubber stopper through which was passed a stainless steel stirrer, thermometer and entry tube for the solution. The whole cell was contained in a perspex box measuring approximately $4'' \times 4'' \times 6''$, through which water was circulated by a centrifugal pump.

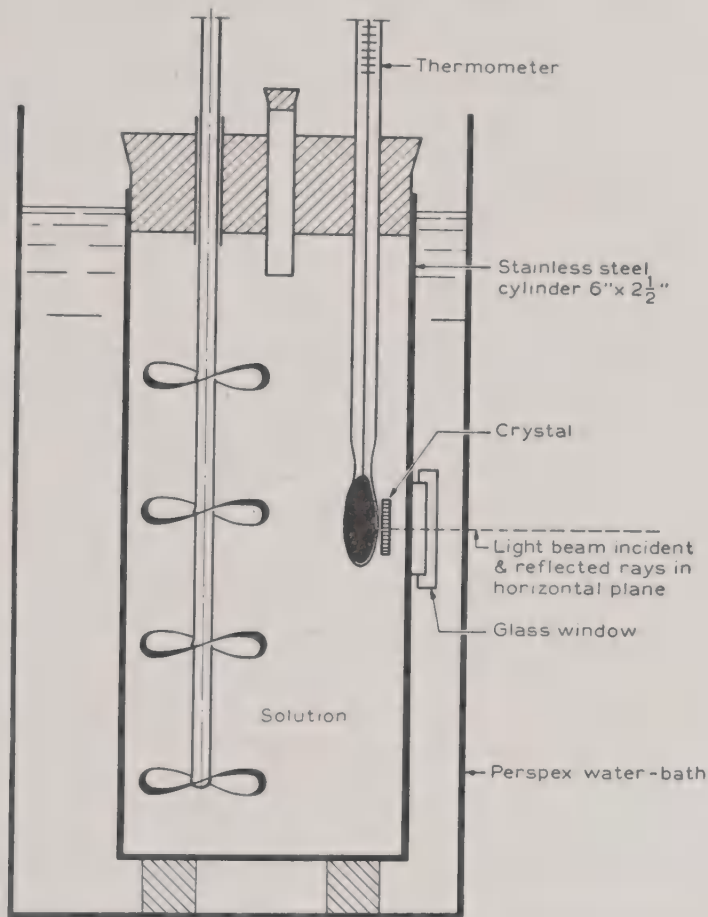


Fig. 2/2. Apparatus similar to unit used by WISE and NICHOLSON for measuring saturation temperatures.

A conical flask which could be heated or cooled was included in the system of circulating water and used for adjusting the temperature of the sucrose solution in the cell. Very little lag was observed by these workers between the temperature of the well stirred sucrose solution and that of the circulating water.

On the outside of the perspex box was a slit formed by two razor blades behind which was placed a 40 W lamp. When the cell was assembled a sucrose crystal was clipped to the thermometer with a rubber band. The

saturation temperature was observed when in viewing the slit behind the crystal the angle of reflection suddenly changed. The solution could be heated or cooled through the saturation temperature a number of times and the average value determined. These workers were able to obtain agreement of temperature readings to within $0.1\text{--}0.2^\circ\text{C}$. The rates of heating or cooling were 1.5°C per minute which was found by test to be satisfactory for the system.

Whilst WISE and NICHOLSON initially used this method for pure sucrose solutions they have subsequently reported results for potassium chloride – sucrose – water solutions⁴. The results for this system differ slightly from those recorded by SHUKOW¹⁴ and are included here in Table 1 (*q.v.*), although the differences are due partly to a lower value for the solubility of sucrose in water.

The advantage which WISE and NICHOLSON claim for this method is that results may be obtained very quickly and hence the possibility of inversion of sucrose taking place is minimised. This is particularly important at high temperatures. The method would appear to be applicable to samples of molasses if the cell were reduced in depth and a higher powered light used for illumination. To obtain a thin enough cell for dark coloured samples of molasses might well require the use of a thermocouple junction instead of the more bulky conventional type of thermometer bulb.

Another method which has been explored as a possible means for identifying the saturation temperature has been described by DOSS, GUPTA and VISHNU¹⁵. These workers have explored the possibility of a break at saturation in the viscosity or electrical conductivity relationship with temperature on a $\log \nu$ $1/T$ plot for molasses. No break was observed for the former but a small one was observed for the latter. The break, however, was not definable with sufficient precision to be worth using as a means for determining the saturation temperature.

3. Three Component Sucrose Solutions

When a third component (or further additional components) may be present in a solution of sucrose and the sucrose is the solute of primary interest, then we speak of the solution as being 'impure' with respect to sucrose. If we consider only the weight relationships of the various components this does not convey information of very much value when considering solubility behaviour. If, however, we consider relationships on the basis of weight of solute per unit weight of solvent a much more satisfactory picture may be obtained of the solubility conditions. In the field of sugar literature it is

TABLE 1

SOLUBILITY OF SUCROSE IN POTASSIUM CHLORIDE SOLUTIONS⁴

Conc. of KCl (g/100 g H ₂ O)	Sucrose solubility (g/100 g H ₂ O), temperature in °C							Solubility coefficient; temperature in °C						
	25° C	30° C	35° C	40° C	45° C	50° C	55° C	25° C	30° C	35° C	40° C	45° C	50° C	55° C
0	205.4	214.5	224.3	234.9	246.5	259.2	273.0	1.003	0.995	0.995	0.994	0.995	0.995	0.996
1	206.1	213.5	223.1	233.5	245.2	257.8	272.0	1.007	0.998	0.993	0.990	0.991	0.991	0.994
2	206.8	214.1	222.8	232.6	244.2	256.8	271.3	1.011	1.002	0.994	0.991	0.988	0.988	0.993
3	207.6	214.8	223.0	232.8	243.6	256.2	271.1	1.014	1.005	0.996	0.993	0.990	0.988	0.995
4	208.3	215.5	223.5	233.2	244.0	256.2	271.7	1.018	1.008	1.000	0.995	0.992	0.989	0.997
5	209.0	216.1	224.4	233.7	244.5	256.4	272.3	1.021	1.010	1.004	0.998	0.994	0.991	1.001
6	209.7	216.5	225.2	234.4	245.0	256.9	273.2	1.024	1.015	1.007	1.001	0.997	0.993	1.004
7	210.3	217.6	225.9	235.1	245.7	257.4	274.0	1.027	1.017	1.010	1.003	0.998	0.995	1.007
8	211.0	218.2	226.6	235.7	246.0	258.0	275.0	1.034	1.024	1.016	1.009	1.003	1.001	1.014
10	212.3	219.6	227.8	236.9	247.2	259.5	276.9	1.050	1.039	1.029	1.022	1.014	1.017	1.033
15	215.6	222.9	230.9	240.1	250.0	263.7	281.9	1.065	1.054	1.043	1.035	1.027	1.035	1.048
20	218.8	226.1	234.0	243.0	253.2	268.4	286.2	1.068	1.068	1.057	1.048	1.041	1.054	1.072
25		229.1	237.1	246.1	256.7	273.1	292.8							
30		231.6	240.0	249.0	261.2	277.7			1.080	1.070	1.060	1.060	1.071	

common practice to refer to the solubility of sucrose as g sucrose/g water, or g sucrose/100 g water. This is not fundamentally different from the practice of physical chemists to refer to solutions in terms of molal concentrations (*i.e.* g. moles of solute/1000 g water). Multiplying by a factor of 2.92 will convert values in g sucrose/g water into molal concentrations.

When a third component is added to a saturated solution of sucrose it may either increase or decrease the solubility. Occasionally there may be no significant influence, and very occasionally a double compound may be formed. The subject of double compound formation will be discussed more specifically at a later stage in this chapter.

When two (or more) solutes are present in solution it has been common to think of them as competing for the solvent, and one solute is said to 'salt-in' or 'salt-out' a second solute according to the change in solubility of the second solute in the presence of the first. In measuring the salting-out effect of solutes which reduce the solubility of the second solute it has been reasonably satisfactory to interpret results in terms of net achievement in competition for solvent molecules. Unfortunately this concept breaks down in circumstances where salting-in or increase in solubility takes place. LONG and McDEVIT¹⁶ extensively reviewed literature relating to theoretical explanations for salting-in and salting-out behaviour, and while drawing attention to the inadequacy of the solvation theory to explain salting-in effects and to its deficiencies in explaining salting-out effects, no comprehensively applicable explanation could be suggested for the various types of behaviour which had been observed. Attention may, however, be drawn to the fallacy sometimes evident in discussion on theories of molasses formation that salting-in behaviour is related to double compound formation.

The subject of salting-in or salting-out behaviour may be considered on a quantitative basis by calculating a 'solubility coefficient' which may be defined as follows.

$$\text{solubility coefficient} = \frac{\text{solubility of solute in impure solution at temp. } t^0}{\text{solubility of solute in pure solvent at temp. } t^0} \quad (1)$$

The figure so obtained for the solubility coefficient (S.C.) will be numerically the same irrespective of whether solubilities are measured in g solute/g solvent; g solute/100 g solvent or in molalities, provided consistent units are used in each case.

The theoretical treatment which various workers have been able to use

when considering the salting-in or salting-out effects of electrolytes on non-electrolytes¹⁶ have not been applicable to sucrose solutions owing no doubt to the high concentration of non-electrolyte in these cases, whereas the theoretical treatments have been more successful when dealing with low solubility non-electrolytes such as the gases.

In Figure 2/3 are illustrated in graphical manner the influence of some secondary solutes on the solubility of sucrose. The solubility coefficient of sucrose is plotted as ordinate and the 'purity' of the solution with respect to sucrose (*i.e.* sucrose/100 total dissolved solids) is plotted as abscissa.

It would appear possible to generalise to this extent that solutes which form a hydrate have a salting-out effect on sucrose at least within the temperature range over which the hydrate is stable whereas those which do not form a hydrate increase the solubility of sucrose¹⁷.

It is also interesting to note the effect of sucrose on the solubility of other solutes. Some illustrations are given in Fig. 2/4 where in this case the abscissa is in terms of g second solute/100 g total dissolved solids. Generally it appears that solutes which increase the solubility of sucrose also have their own solubility increased and *vice versa*. Two exceptions to this generalization are shown in Fig. 2/4 *viz.* fructose and ammonium nitrate. Also fructose normally crystallises in the anhydrous form at 30° C, but at this temperature it has a slight salting-out effect for sucrose.

JACKSON and SILSBEE¹⁸ determined the solubility of sucrose in invert sugar solutions and the data in Table 2 have been prepared from their results.

The system containing invert sugar in solution as well as sucrose is, however, not a three-component system and the two reducing sugars – glucose and fructose – will each have their own individual influence on the solubility of sucrose. KELLY¹⁷ found that whilst both reducing sugars exercised a

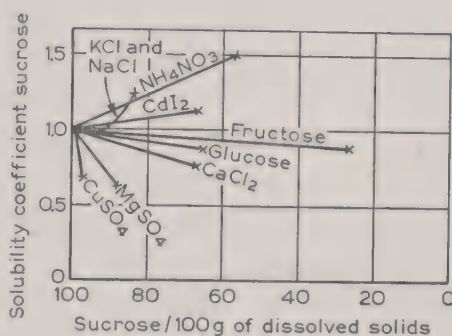


Fig. 2/3. Influence of second solute on the solubility coefficient of sucrose; *J. Appl. Chem. London* 4 (1954) 411.

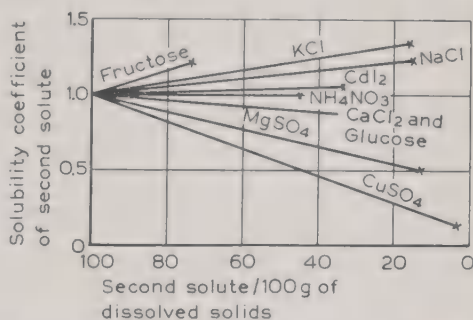


Fig. 2/4. Influence of sucrose on the solubility coefficient of the second solute; *J. Appl. Chem. London* 4 (1954) 411.

TABLE 2
SUCROSE IN INVERT SUGAR SOLUTIONS¹⁸

Conc. of invert sugar (g/100 g water)	Solubility of sucrose (g/100 g water)			Solubility coefficient		
	23.15° C	30° C	50° C	23.15° C	30° C	50° C
0	208	219	260			
50	187	197	242	0.90	0.90	0.93
100	171	182	222	0.82	0.83	0.85
150	158	170	216	0.76	0.78	0.83
200		159	208		0.73	0.80
250		152	201		0.69	0.77
300		146	194		0.67	0.75
350		143	192		0.65	0.74
400		141	189		0.64	0.73

salting-out influence on sucrose, the influence of glucose was a little greater than that of fructose at 30° C. This was consistent with the observation that glucose normally crystallises as the monohydrate at this temperature whereas fructose crystallises in the anhydrous form. These results are generally in agreement with those obtained by workers who have examined sucrose solubility relationships in natural molasses and reached the conclusion that the reducing sugars lower the solubility of sucrose. THIEME⁷ in fact obtained very close correlation between the reducing sugar content of Java molasses and the solubility of sucrose.

When discussing solubility relationships in natural molasses it has frequently been stated in the literature that inorganic solutes increase the solubility of sucrose and in this respect are in contrast to the influence of the reducing sugars. A close examination of results from synthetic systems containing sucrose and an inorganic solute reveals, however, that there are many exceptions to this view. Even in the results of SHUKOW¹⁴ published in 1900 the presence of potassium chloride in concentrations up to about one third of that required to saturate the solution at 30° C actually reduced the solubility of sucrose. This was confirmed recently by KELLY¹⁷ and also by WISE and NICHOLSON⁴. SHUKOW's results also showed similar behaviour with potassium bromide, potassium nitrate, and sodium chloride. KELLY has found that salts which form hydrates such as calcium chloride, magnesium sulphate and copper sulphate have a marked salting-out effect.

KÖHLER¹⁹ examined solutions saturated with both sucrose and a second solute at a temperature of 31.25° C, and he also found the solubility of sucrose to be reduced in the presence of such solutes as calcium chloride, calcium acetate, sodium sulphate, magnesium sulphate and potassium sulphate.

It is evident, therefore, that it is essential to take into consideration the nature of the inorganic constituents of a molasses in addition to their concentration.

There is one constituent which is peculiar to and important in beetsugar materials, *viz.* raffinose. The solubility of sucrose in the presence of raffinose has been examined by MARIANI and CIFERRI²⁰ at temperatures of 25° and 64° C. At the higher temperature a well defined salting-out of sucrose was indicated with a minimum S.C. of 0.78 when the solution was saturated with respect to both solutes, whereas at 25° C the S.C. reached a minimum of 0.92. This reciprocal temperature coefficient of the solubility coefficient whilst being very marked in this system may also occur in other systems to a greater degree than had previously been considered likely. There is a trend in this direction in the system containing potassium chloride as may be evidenced from the data in Table 2.

4. Multi-Component Sucrose Solutions

Natural molasses is a multi-component system with a high degree of complexity. Although samples have been analysed for many years, the full number of components is still incompletely identified. The nature of many of the components as well as their concentration vary from place to place and from one season to another. One method of investigation is to analyse the behaviour of molasses itself and compare the results from samples with and without some particular component or group of components. This is the line of approach which has been most generally adopted by research workers in this field in different parts of the world. The satisfactory analysis of results has, however, been a major obstacle to progress and from time to time some workers have given attention to studies of synthetic solutions prepared from pure materials.

The greatest amount of satisfaction is likely to be obtained by combining the results from these two lines of approach. Unfortunately it is seldom possible to remove completely a single specific component from a sample of molasses and to examine behaviour before and after such a procedure; it is also extremely unusual for two samples of molasses to agree completely in composition with the exception of a single constituent. One can only aim for the best approach under the circumstances experienced by the investigator and interpret results with appropriate precautions and restraint in generalising.

Similar comment might well be applied to the results of work in the field of synthetic solutions. It should be obvious that a study of the behaviour

of some particular component would be far more valuable from the point of view of practical application if as many as reasonably possible of the other components normally found in practice are also present.

Perhaps the most satisfactory compromise between these two lines of approach is to study a sample of natural molasses known to be deficient in a particular component and to observe any change in behaviour after adding varying quantities of this component in a pure form.

KELLY has used this third line of approach to study the change in solubility of sucrose with different types of molasses²¹. These results provide a picture of the range of behaviour which can be experienced under varying conditions of temperature and purity. In Fig. 2/5 the results are illustrated for four different types of behaviour.

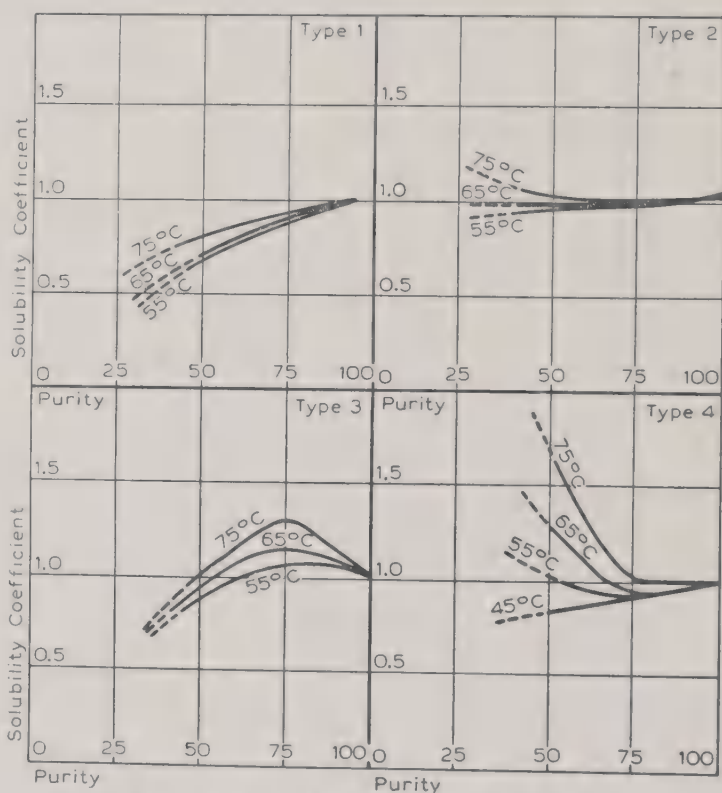


Fig. 2/5. Solubility coefficient variations in molasses.
Proc. Queensland Soc. Sugar Cane Technologists 13 (1946) 135.

In the first type it can be seen that the solubility coefficient of sucrose falls steadily with decreasing purity. This type of behaviour is characteristic of a predominating influence of reducing sugars. Whilst this is more generally the simplest interpretation of results of this character, the possibility of other non-sucrose solutes or combinations of solutes exercising a similar

influence or at least a complementary influence must not be overlooked.

In the fourth type we see an almost completely contrasting type of behaviour in which the solubility coefficient of sucrose increases over a wide range of conditions. At saturation temperatures of 65–75 °C the rate of increase of the solubility coefficient as the proportion of impurities increases is very substantial. The behaviour depicted in the fourth type of molasses is characteristic of a predominating influence of inorganic solutes with chlorides more influential than sulphates. It is not sufficient to inspect only the total sulphate concentration in the molasses impurities as there may well be much of it in the form of gypsum crystals which would have no direct influence on the solubility characteristics of sucrose.

In the behaviour observed with the second and third type of molasses illustrated, it is difficult to make a general statement concerning the possibility of any one component or group of components exercising a predominating influence.

One characteristic which is reasonably well shared by all four types here illustrated is the general fall in solubility coefficient of sucrose at low saturation temperatures as the proportion of impurities increases. KELLY believes this to be related more to the influence of glucose in the reducing sugars and its ability to crystallise as a monohydrate. This view is based on observations of sucrose solubility changes in synthetic solutions containing only sucrose and the two reducing sugars, either with or without an inorganic solute.

Most of the measurements of the solubility of sucrose in molasses have been made as part of an investigation into the purity limits to which crystallisation of sucrose might be taken. There seems to be general agreement that good exhaustion is more frequently associated with conditions under which the solubility of sucrose is reduced by the combined influence of associated non-sucrose solutes. This can be readily understood especially when behaviour is as illustrated by the type 1 molasses depicted in Fig. 2/5. Poor exhaustion could also be readily explained for conditions simulating those experienced with the type 4 molasses when operating at high saturation temperatures. The greatest difficulties in interpreting factory operating results would seem to be associated with endeavours to take advantage of apparently more favourable conditions at lower operating temperatures without the expected corresponding benefits materialising. The reasons which have been suggested from time to time include the difficulties of operating with highly viscous materials at low temperatures or the possibilities of double compound formation with sucrose. This chapter, however, is intended to deal more specifically with solubility conditions.

The solubility of sucrose in pure solutions has also been studied in the presence of more than one other solute. The conditions which have received the most attention are the solubility values in the presence of invert sugar. PRINSEN-GEERLIGS²² was an early worker in this field and he concluded that the presence of invert sugar was without influence upon the solubility of sucrose. In his experiments he used oversaturated solutions of sucrose and from a study of the conditions under which he examined the system it is considered probable that the solutions were oversaturated with respect to sucrose even at the end of one month – the time allowed by GEERLIGS to reach equilibrium. Later more satisfactory sets of data were obtained by VAN DER LINDEN²³ and by JACKSON and SILSBEE¹⁸. Both of these workers found that invert sugar caused a marked reduction in the solubility of sucrose, although the figures obtained by the latter workers indicated a slightly higher degree of salting-out of sucrose especially at 50° C. JACKSON and SILSBEE also continued their investigations to cover other conditions of reducing sugar concentration by altering the composition of the invert sugar solutions which they prepared. This was done mainly by evaporation and removal by crystallisation of glucose-hydrate. This work was most painstakingly conducted and appreciable ingenuity was required to overcome the difficulty of not having fructose available in crystalline form.

More recently KELLY has had the opportunity to investigate this system at 30° C using crystalline samples of the three sugars as starting materials²⁴. The relative effects of these sugars upon each other's solubility is illustrated in Fig. 2/6 using trilinear coordinates to represent the relative proportions of each of these solutes. Lines have been drawn to join points of equal solubility coefficient. KELLY found that the behaviour of glucose was not as simple as had previously been thought to be the case and that even at 30° C crystalline anhydrous glucose was observed as a stable solid phase in equilibrium with solutions of a significant range of composition, and as a meta-stable phase over a very much wider range of conditions. The highest degree of salting-out of sucrose was observed about mid-way between the two meta-stable quaternary points of the system and when the concentration of glucose slightly exceeded the concentration of fructose.

It is interesting to note that in certain regions of high concentration of solute there is a small salting-in effect, and at the main quaternary point each of the three solutes shows a solubility coefficient in excess of unity, namely 1.08 for sucrose, 1.11 for fructose and 1.26 for glucose. Sucrose shows two points of low solubility coefficient with a value of 0.625 at point *M* (*q.v.*) and the second with a value of 0.66 at point *N* when the solution was saturated with both sucrose and fructose, with a relatively small proportion of glucose.

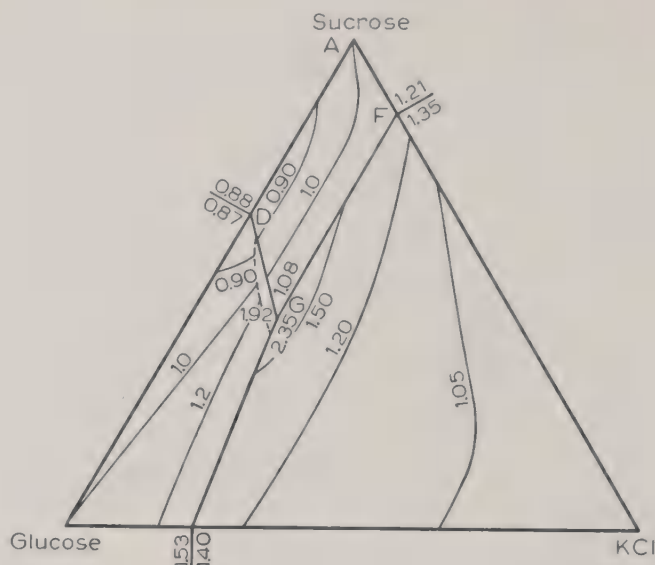


Fig. 2/8. Solubility-coefficient relationships for the quaternary system sucrose-glucose-KCl-water; *J. Appl. Chem. London* 5 (1955) 69.

coefficient conditions are illustrated for these two systems. The area $ADGF$ of Fig. 2/8 where glucose is the reducing sugar could be superimposed upon Fig. 2/7 in which fructose is the reducing sugar. In other words, the influence of glucose in the presence of potassium chloride on the solubility of sucrose is almost identical with the influence of fructose in the presence of potassium chloride until the condition is reached where the solution is also saturated with glucose.

It is now possible to prepare a diagram from the examination of synthetic solutions of pure compounds and to compare this with the diagrams of Fig. 2/5 for natural molasses. In Fig. 2/9 has been plotted the relationship between the solubility coefficient with respect to sucrose for solutions of

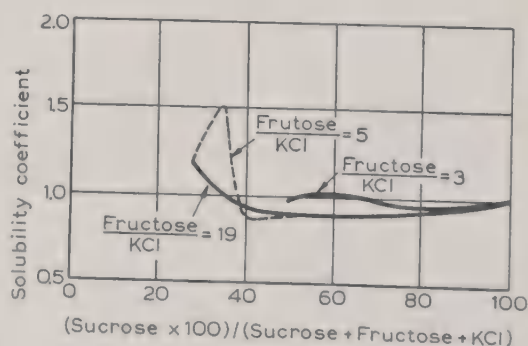


Fig. 2/9. Change of solubility coefficient accompanying isothermal crystallization of sucrose in the quaternary system sucrose-fructose-KCl-water; *J. Appl. Chem. London* 4 (1954) 411.

gradually falling purity in the system sucrose – fructose – potassium chloride – water. The reducing sugar – fructose – has been preferred on this occasion because of its greater solubility than glucose and the consequent wider range of ‘purity’ conditions which can be examined before the system is saturated also with respect to reducing sugar.

This simplification is considered permissible in view of the very close similarity between the influence of fructose and glucose on the solubility of sucrose in the presence of potassium chloride. Three conditions are illustrated with ratios of fructose to potassium chloride (*cf.* R.S./ash in molasses) of 3, 5 and 19. A further comparison between behaviour of sucrose in a synthetic system and in natural molasses will be given at a later stage in this chapter when discussing conditions in terms of phase equilibrium diagrams.

Increasing the number of solutes in a solution also has the effect of increasing the total concentration of solids which may be dissolved in a particular amount of water. As we have been referring to solubility in terms of weight of solute per unit weight of water it is interesting to speculate on the amount of solute which a unit weight of water can dissolve as the number and variety of solutes are progressively increased.

Thus at 30° C one gram of water will dissolve 2.19 g of sucrose, or 7.3 g of solute when made up of sucrose and fructose. If glucose is added to provide a solution saturated with respect to all three solutes, a total solute concentration of 8.8 g will be reached for every g of water. Had potassium chloride been the third solute instead of glucose then the total solute concentration would have reached a maximum of 9.0 g/g water. The solubility of potassium chloride is itself slightly lower than that of glucose, but its stronger salting-in effect results in a higher total solids content. It was interesting to observe that the conditions of maximum dissolved solute did not coincide with the quaternary point but were associated with a range of conditions surrounding the quaternary point. The system containing all four solutes in solution has also been studied by KELLY²⁶ and it was found that with sucrose, fructose, glucose and potassium chloride all dissolved to give a solution of maximum total solids concentration it was not possible to increase this value beyond the figure of 9.0 g/g water.

It can be seen therefore that the total concentration of dissolved solids in a sucrose solution may be increased more than fourfold by increasing the number of solutes present in solution. Thus the ‘purity’ of a solution saturated with respect to sucrose has been ‘reduced’ to a figure as low as 21 % by a process which amounts to dilution with additional solutes. There would appear to be no theoretical limit to the number of solutes which

could be dissolved in the same unit weight of water although the total weight of solutes might not exceed nine times the weight of the water.

When considered on a molar basis the highest number of moles of solute dissolved in a mole of water was experienced in the sucrose – fructose – potassium chloride system when up to 1.3 moles of solute were dissolved in a mole of water at 30° C. The maximum reached for a solution saturated with sucrose in the five component system was approximately one mole of solute per mole of water. This represents a total molality of 55.5.

Although solutions were obtained with more moles of solute than of solvent, the water was still strictly the true solvent as no individual solute reached a concentration of one mole. Fructose, however, was frequently close to reaching this figure and would exceed it at higher temperatures. Fructose alone would reach this condition at approximately 70° C according to tables for the solubility of fructose in water prepared by the *U.S. National Bureau of Standards*¹⁸. In the presence of solutes exercising a salting-in effect, fructose would become the true solvent at temperatures even lower than 70° C.

Conditions of this nature have not as yet been identified in natural molasses.

5. Sucrose Double Compound Formation

In the study of natural molasses the possibility of sucrose forming double compounds with other solutes occurring therein has been consistently considered for many years. PRINSEN-GEERLIGS²² has been the strongest protagonist for this view and in fact defined molasses as 'a hydrated syrupy-liquid combination of sucrose and salts'. He did himself claim to have prepared certain of these compounds²⁷. HELDERMAN on the other hand²⁸ strongly contested the view on the basis of his own experiments. Under pressure from PRINSEN-GEERLIGS²⁸ he conceded the possibility of such compounds existing²⁹ but reconfirmed his own inability to crystallise any. KOLTHOFF³⁰ later re-opened the subject by claiming that HELDERMAN had not waited long enough for the double compound to form.

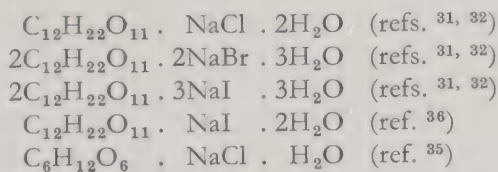
Perhaps the most important investigation of sucrose double compounds and probably the most painstaking is the one recorded by GILL³¹ in 1871. This work does not seem to have been noted by the workers in Java in the first quarter of the present century.

GILL actually crystallised double compounds of sucrose with sodium chloride, sodium bromide and sodium iodide. More recently several of these, and especially the double compound with sodium bromide have been crystallised by BEEVERS and COCHRANE³² and studied by X-ray

diffraction experiments. KELLY has also crystallised a double compound with sodium iodide³³.

HELDERMAN was also unsuccessful in his attempts to crystallise double compounds with glucose and NaCl³⁴ but subsequently MATSUURA³⁵ reported successful identification of a double compound between these two substances.

The following formulae have been attributed to double compounds by various workers in this field



Perhaps the most important reason for including a section on double compound formation in a chapter on solubility determination is the fact that PRINSEN-GEERLIGS²² considered the property of salting-in of sucrose to be associated with the ability for sucrose and the particular salting-in compound to form double compounds themselves. He expressed the view that the postulated hydrated double compounds with inorganic salts also increased the solubility of sucrose. This, however, is by no means consistent with a solubility figure determined by GILL³¹ for the sucrose-sodium iodide crystals which he obtained. He reported that these crystals dissolved in 1.5 times their own weight of water at room temperature. If this concentration be calculated in terms of sucrose solubility, a very substantial reduction is indicated. For example a solubility coefficient of 0.18 would be indicated if 'room temperature' is taken as 20° C or 0.19 if it is 10° C. As the double compound with sodium iodide is the most easily crystallised of the sucrose double compounds it is not thought to be very good evidence for the existence of double compounds simply that the solubility coefficient for sucrose should be increased.

More recently WIKLUND³⁶ has given attention to ways and means for establishing or otherwise the existence of double compounds by the measurement of other physical properties of sucrose systems containing three or more components. In particular he has employed JOB's principle to interpret the modification of the optical rotation of sugar solutions caused by salts on the basis of possible double compound formation. Another approach has been the one made by VAN HOOK³⁷ to examine X-ray scattering patterns of a desiccated mixture of sucrose and potassium nitrate in equimolar proportions. Under these conditions a complete amorphous

pattern was realised whereas a pattern characteristic of potassium nitrate with no marked evidence of sucrose was obtained when the salt was in molar excess. Also KELLY has observed abnormal viscosity behaviour³⁸ of certain impure sugar solutions which could be combined with observations of electrical conductivity⁹ to interpret conditions as favouring double compound formation. The fact remains, however, that whereas a few double compounds of sucrose have been crystallised from synthetic solutions under special conditions, the most characteristic property of molasses is that it does not crystallise. KELLY therefore feels justified in emphasising the need for very great caution when interpreting solubility data in terms of double compound formation.

When carrying out experiments with the object of actually crystallising double compounds of sucrose from synthetic solutions one of the most important attributes needed by the experimenter is a large measure of patience. This was a feature of the work carried out by GILL³¹ it was a major deficiency of HELDERMAN's work²⁸ according to KOLTHOFF³⁰ and in the only experiments with which KELLY has achieved success in crystallising a double compound with sodium iodide it was necessary to allow the process to continue over a period of about six months³³.

6. The Phase Rule and Phase Equilibrium Diagrams

The possibility of employing a phase rule approach to the study of natural systems containing sucrose in solution, of which cane and beet molasses are the examples of most widespread interest, has intrigued scientific workers in this field for many years. In 1915 VAN DER LINDEN³⁹ drew attention to such a possibility and discussed the subject of molasses formation from the standpoint of the phase rule. He discussed the subject in terms of a system sugar – water – non-sugar, representing the non-sugars as a single component. HELDERMAN²⁹ also conducted investigations which he interpreted with the aid of phase rule considerations.

Unfortunately at that time the issue became rather confused with the acceptability or otherwise of various theories of molasses formation. For example, PRINSEN-GEERLIGS²⁷ held strongly to his definition of molasses as a hydrated combination between sugar and salts, which cannot be broken up by dissociation in a concentrated state and therefore cannot yield sucrose in a crystallised form. On the other hand VAN DER LINDEN defined molasses as a mixture which is saturated not only with respect to sucrose but also with respect to at least one more substance. Although use of the phase rule and phase equilibrium diagrams should have been of assistance to differen-

tiate between these two theories, the fact that protagonists of a phase rule approach failed to identify, specific double compounds with sucrose brought disrepute upon this line of approach in the eyes of PRINSEN-GEERLIGS and his supporters. Both VAN DER LINDEN and HELDERMAN seem to have bowed to the dominance of PRINSEN-GEERLIGS and withdrew from the field with insufficient data to substantiate any alternative viewpoint.

And then in 1935 MICHELI and DE GYULAY⁴⁰ discounted the possibility of obtaining useful information regarding the limitation of sucrose crystallisation in molasses from a phase rule approach. They suggested that under factory conditions of operation, sufficient time is not available for the molasses and crystal in a low grade molasses to reach equilibrium at the end of cooling in the crystallisers. This type of emphasis later found its scientific development in the kinetic studies of VAN HOOK⁴¹, DUNNING⁴² and others.

Irrespective of the relative merits of the various theories of molasses formation a study of molasses should be of interest from the point of view of the phase rule. There is no doubt that molasses is frequently saturated with respect to a second solute as VAN DER LINDEN suggested. Examples of such include the identification of such crystalline substances as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), potassium chloride⁴³ or calcium aconitate⁴⁴, but there is no evidence that under the circumstances of their appearance they have of themselves limited the crystallisation of sucrose. On the other hand, there is no doubt that sucrose will, at least occasionally, form double compounds with inorganic salts^{31, 32}. But the fact remains that no one has yet been successful in crystallising a double compound of sucrose from either sugar beet or sugar cane molasses. We must also not overlook the importance of the time factor in these investigations as those double compounds of sucrose which have been crystallised required a very long period for successful achievement. KOLTHOFF³⁰ drew attention to this weakness in the work of HELDERMAN. Also there is no doubt from the work of VAN HOOK⁴¹ and others that the rate of crystallisation of sucrose can be appreciably reduced by the presence of other solutes, and under certain conditions it may be very difficult to be certain that equilibrium conditions have been established.

At the time when VAN DER LINDEN and HELDERMAN were discussing the application of phase rule considerations they were appreciably limited by the amount of factual information available.

The phase rule was first enunciated by GIBBS in 1874 when he defined conditions of equilibrium in a heterogeneous system as a relation between the number of *phases* and the *components* of the system. Although a phase must be physically homogeneous, it need not be chemically simple. The

compounds of a system are defined as the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be defined.

In the process of crystallising sucrose we are interested in a 'phase reaction'. The process of evaporation is also a phase reaction which indirectly influences the crystallising process. Under conditions of evaporation in a vacuum pan at a particular vacuum we have for a substantial period during the boiling of a strike, conditions of almost isothermal crystallisation. As boiling continues in the final stages of the process the temperature rises by an amount equivalent to the change in boiling point elevation brought about by increasing the total concentration of dissolved solids. In the crystallisers on the other hand crystallisation is polythermal with falling temperature conditions and also reheating but the total water concentration remains constant unless dilution is practised.

In order to obtain the best understanding of behaviour of molasses, which we know is a very complex multicomponent system, it is preferred to build up gradually from systems of minimum complexity. In this study the system water – sucrose is worth a primary consideration. This is tantamount to studying the solubility of sucrose in water, a subject which is not strictly within the scope of the present chapter, but one which cannot be avoided completely as we are not able to express solubility coefficients or saturation coefficients accurately unless we have satisfactory basic reference figures for calculation purposes.

Unfortunately there is a diversity of information concerning the solubility of sucrose in water from the earliest data of FLOURENS (1876) and HERZFELD (1892) to the most recent of TAYLOR (1947) and of WISE and NICHOLSON (1955). The information to 1940 has been summarised by KASJANOV⁴⁵ and tabulated by the U.S. BUREAU OF STANDARDS⁴⁶. Values from 0° C to 144° C have been set out by HIRSCHMÜLLER¹.

There have been two general endeavours to express the solubilities mathematically by means of algebraical expressions. The type most commonly favoured summarises the results of HERZFELD, TAYLOR and of WISE and NICHOLSON in equations (2), (3), and (4). Recently VAVRINECZ⁴⁷ has reviewed existing solubility data and found that equation (5) fits these to yield a figure with an error of ± 0.094 .

$$C = 64.18 + 0.134t + 0.000531t^2 \quad (2)$$

$$C = 63.608 + 0.1322t + 0.000722t^2 \quad (3)$$

$$C = 62.77 + 0.1706t + 0.000344t^2 \quad (4)$$

$$C = 64.47 + 0.10336t + 0.001424t^2 - 0.000006020t^3 \quad (5)$$

where

C = saturation concentration (g sucrose/100 g of solution)
 t = centigrade saturation temperature.

GRUT⁴⁸, however, when examining impure solutions of sucrose, molasses and solutions of pure sucrose itself found that he could express solubility of sucrose in the general manner illustrated by equation (6).

$$e = a(b - t) \tag{6}$$

where

e = g H_2O /100 g sucrose
 t = centigrade saturation temperature
 a and b = constants characteristic of the system.

For pure sucrose solutions he found $a = 0.3901$ and $b = 147.47$.

When considering either of these two forms of equations there is a strong temptation to extrapolate to conditions beyond those covered by the investigation. This especially applies, for example, to determining what might be termed the ‘apparent melting point’ of sucrose. This may be done

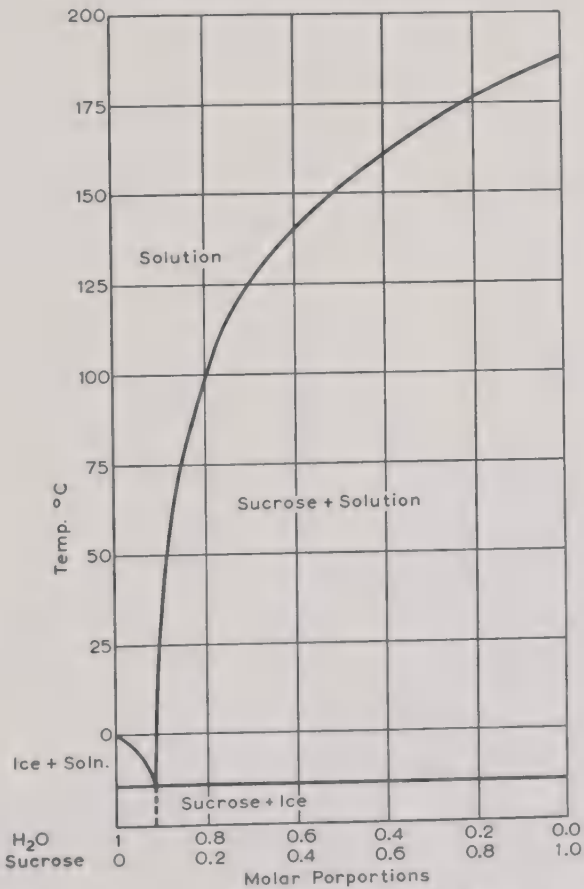


Fig. 2/10. Solubility-temperature relation in the sucrose-water system.

from the first set of equations by making $C = 100$, or from the GRUT type of equation by making $e = 0$. WISE and NICHOLSON⁴ have drawn attention to difficulties which might be experienced in doing this with expectation of an accurate result. At first sight the extrapolation from 80% to 100% of concentration appears to be not unreasonable. However, a concentration of 80% sucrose corresponds to a mole fraction of sucrose of about 0.17. To obtain the melting-point it is necessary to extrapolate to a mole fraction of 1.00.

In Fig. 2/10 the results of as wide a range as possible of sucrose solubility data have been plotted on a molar basis giving us what amounts to a phase equilibrium diagram for the system from one mole of water at the left hand end of the abscissa through all proportions of the two substances to one mole of sucrose at the right hand end. For the convenience of comparison, Fig. 2/11 has been drawn with the temperature-solubility curve for sucrose expressed as g/100 g solution. Recently VAVRINECZ⁴⁹ has also reviewed the literature and prepared a phase diagram from -30°C up to the melting-point of sucrose.

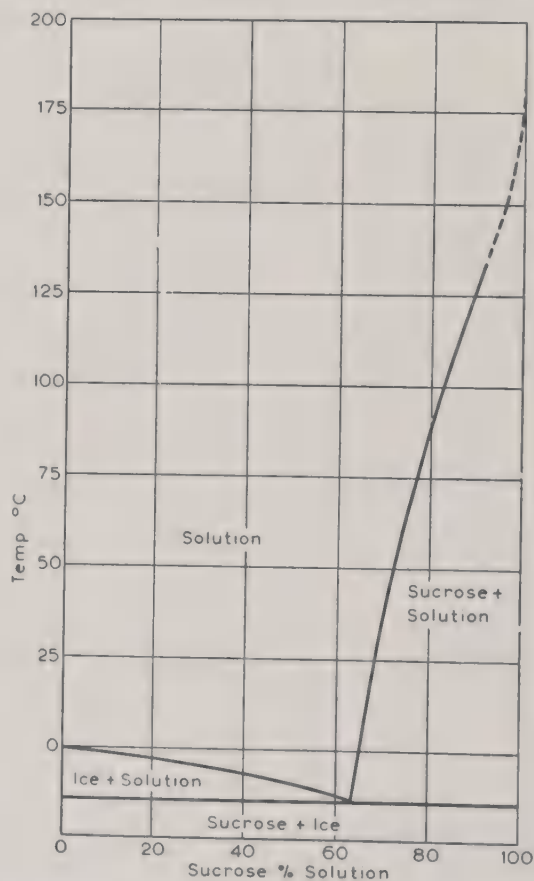


Fig. 2/11. Solubility-temperature relation in the sucrose-water system.

For data at the low temperature end, use has been made of the work of YOUNG and JONES⁵⁰ who studied the crystallisation of sucrose hydrates. The diagram as illustrated here is very much simplified showing only a single eutectic between ice and sucrose, whereas two hydrated crystalline phases of sucrose were definitely identified (*viz.* the hemiheptahydrate and hemipentahydrate) and possibly six other phases. In actual fact the simple eutectic was never really obtained experimentally, but is perhaps a justifiable simplification for the present considerations. In the higher temperature range of their experiments (10–40° C) the data of YOUNG and JONES merge more smoothly into the data of HERZFELD, with the values for WISE and NICHOLSON showing the greatest divergence. Over the temperature range from 30° to 80° C the differences are not great. At the high temperature end (*i.e.* temperatures above 100° C), BENRATH⁵¹ is the only worker who has ventured far into this region. He has, however, had fairly wide experience in the study of solubilities of inorganic and organic solutes in water at temperatures above 100° C, and his results should be considered seriously. At the low temperature end of BENRATH's results values merge with those of FLOURENS at 100° C with HERZFELD and GRUT showing higher solubility values.

By including conditions up to the highest saturation temperature recorded by BENRATH (144° C for 94% sucrose solution) the range of data is more than double that mentioned by WISE and NICHOLSON in terms of mole fractions. Thus data are shown to cover the mole fraction range for sucrose from 0 to 0.38. The extrapolation to the melting point of sucrose at m.f. = 1.0 is still a long one, but is nevertheless quite smooth in character to a figure of 188° C.

There is a diversity of information recorded in the literature, particularly in handbooks of organic chemistry, concerning the melting point of sucrose. This subject was reviewed by SHAH and CHAKRADEO⁵² who reached the conclusion after a number of investigations that the numerous references to a m.p. of 160° C were in error and that in fact a figure of 188° C could be obtained quite readily and with very satisfactory reproducibility using sucrose suitably purified by recrystallisation from alcohol. The phase diagram when plotted on a molar basis completely substantiates these views, and calculations of m.p. from the solubility formulae quoted which give much lower values are misleading. It would, however, not be without interest actually to measure saturation temperatures for mole fraction between 0.38 and 1.0, but there would be quite appreciable technical difficulties as the range corresponds to sucrose containing less than 6% of water by weight in the water – sucrose mixture.

GRUT⁴⁸ extended the application of his method of mathematical treatment to samples of beet molasses. He found that as the purity decreased the constant a increased in value, whereas b decreased. The fall in value of b with decreasing purity was consistent with the interpretation that b might represent the melting point of the solute, in that the melting point of impure sucrose would be expected to decrease progressively with increasing amount of impurity until eutectic conditions might be reached. GRUT also found that the product ab was practically constant irrespective of purity. When this is the case then the effects of the impurity on the solubility becomes less and at $t = 0$ the solubility coefficient differs little from unity even for a 60% purity molasses.

KELLY has found the equation of GRUT to be generally applicable to a wide variety of synthetic solutions and also to samples of sugar cane molasses at least over the temperature range 30–70° C. The results of HERZFELD, TAYLOR and of WISE and NICHOLSON can also be cast into this form and very satisfactory straight line relationships indicated. However, KELLY has by no means observed constancy of value for the product ' ab '. It is considered unlikely that solubility coefficient would invariably be unity at $t = 0$, especially in view of the great complexity of the system when sundry hydrated phases may appear.

TABLE 3

CONSTANTS a AND b IN GRUT EQUATION: $e = a(b - t)$, WHERE $e = \text{H}_2\text{O}/100$ SUCROSE AND $t = \text{TEMPERATURE } ^\circ\text{C}$

Substance	a	b	ab
Sucrose (GRUT)	0.3901	147.47	57.52
(HERZFELD)	0.353	158.55	55.96
(TAYLOR)	0.40	147.25	58.90
(WISE and NICHOLSON)	0.396	148.07	58.63
Glucose (20–50° C)	2.26	67.7	153
(50–90° C)	0.519	124.5	64.6
Fructose	0.375	89.0	33.4
Cane molasses			
75 purity, type 1	0.443	149	66
75 purity, type 2	0.453	144	65.3
75 purity, type 3	0.522	121	63.3
75 purity, type 4	0.507	135	68.5
50 purity, type 1	0.739	127	93.9
50 purity, type 2	0.58	124	72.0
50 purity, type 3	0.825	109	90.0
50 purity, type 4	0.87	96	83.2
40 purity, type 1	0.95	120	113.5
Sucrose + fructose (60 + 40)	0.33	140	46
Sucrose + fructose + glucose (60 + 20 + 20)	0.57	130	74.7
Sucrose + KCl (90 + 10)	0.42	136	57.5
Sucrose + NaCl (90 + 10)	0.50	126	62.7

The constants a and b in the GRUT equation have been calculated for a number of different conditions and these are summarised in Table 3. It should be borne in mind that care should be exercised when extrapolating beyond the limits of temperature conditions actually employed to derive the results. As a matter of interest the solubilities of glucose and fructose as recorded by the U.S. NATIONAL BUREAU OF STANDARDS¹⁸ have also been cast in this form.

Throwing the solubility relationships into the form which GRUT has used is equivalent to saying that if solute concentrations at saturation are expressed as molalities (g moles/1000 g water) then the reciprocal of these molalities is inversely related to the absolute temperature. This may be expressed mathematically as in equation (7).

$$\frac{1}{M} = a (T + c) \quad (7)$$

In the case of sucrose equation (8) fits HERZFELD's results over the range 0–100° C.

$$\frac{834}{M} = 432 - T \quad (8)$$

This general relationship (7) appears to fit a number of non-polar organic solutes in water and also some salts such as potassium and sodium acetates, but does not fit inorganic salts which show marked and variable curvature for graphs plotted on this basis.

If we put equation (7) in the general form of equation (9)

$$\frac{1}{M} = \kappa(y - T) \quad (9)$$

then the constant κ may be obtained by multiplying the GRUT constant a by the molecular weight of the solute and by 10^{-5} ; and the constant y by adding 273.1 to the GRUT constant b .

When we add a third component to the water-sucrose system it is most convenient to represent the phase relationships graphically with the aid of tri-linear coordinates in an equilateral triangle. In a graph of this type the sum of the three components is unity (or 100) at all times and then relative proportions are plotted appropriately in the triangle. Each of the three corners represents a pure component, the compositions of mixtures of any combination of two components are represented along the three sides of the

triangle, and mixtures of three components are represented within the area of the triangle. There are two types of diagrams which we may consider (a) an isothermal diagram *i.e.* solubility conditions are at one particular temperature or (b) a polythermal diagram setting out conditions over a range of temperatures which for completeness would extend to the melting points of each of the three components.

The relative proportions of the three components may be expressed in terms of weight percentages with the total in each case being unity or a convenient multiple such as 100. Or they may be expressed on a molar basis representing the mole fraction of each component throughout the diagram. Any combination of the three components may then be represented by a point in the triangle. The distance from the point to any side (measured parallel to either of the others) gives the proportion of the component represented at the opposite corner. If a line is drawn through any corner to a point on the opposite side, then all points on this line represent a constant ratio of the other two components with a changing amount of the component represented at the particular corner concerned. Also a line parallel to one of the sides represents a constant proportion of one component with variable amounts of the others.

As a simple example we can consider the system water-sucrose with potassium chloride as the third component. Double compound formation has not been identified in this system and the phase relationships have been worked out³ at a temperature of 30° C for the full range of solute proportions.

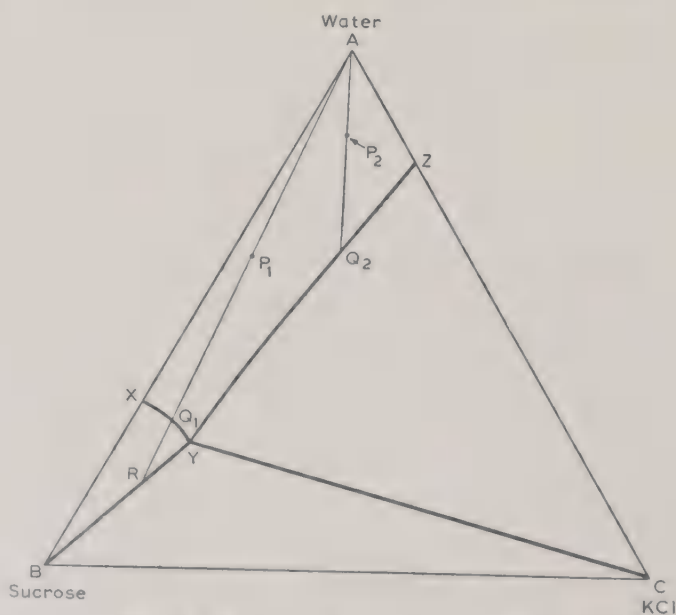


Fig. 2/12. System water-sucrose-KCl.

These are illustrated in Fig. 2/12 with the solvent – water at the apex of the triangle A , pure sucrose represented at the left hand end of the base B and pure potassium chloride at the right hand end of the base C . Point X represents the proportions of sucrose to water (*viz.* $AX : XB$) at the saturation temperature of 30°C , *i.e.* the solubility of sucrose in water. The point Z represents the solubility of potassium chloride in water at 30°C , the relative proportions of solute to solvent being $AZ : ZC$. Point Y within the triangle represents the composition of solution which is saturated with both solutes. This is spoken of as the ternary point of the system at which three phases are in equilibrium and is a point of fixed composition at the stated temperature. Any point along the line XY represents solution saturated with respect to sucrose and any point along ZY represents solution saturated with respect to potassium chloride. Any point within the area XYB represents the composition of solution which would be oversaturated with respect to sucrose or which would be a mixture of solution and crystalline sucrose. Similarly within the area YZC the composition is that of solution oversaturated with respect to potassium chloride or a mixture of solution and crystalline potassium chloride. Any point within the area $AXYZ$ represents solution which is undersaturated with respect to either of the two solutes, and in the area BYC both solutes saturate the solution and crystals of each are also present unless a condition of supersaturation temporarily prevails.

A diagram of this type is suitable for the consideration of conditions of isothermal evaporation, but not for polythermal crystallisation. If for example we have solution of composition corresponding to point P_1 and carry out evaporation then the composition of the solution will change along an extrapolation of line AP_1 . Evaporation will continue until the composition reaches that corresponding to the intersection of extrapolated AP_1 with XY , and we can call this point Q_1 . When the composition reaches Q_1 , conditions satisfactory for the crystallisation of sucrose have been reached. If evaporation is continued and crystallisation is maintained then the composition of the system will continue to change along the line Q_1R , but the liquid phase will change in composition along the saturation line Q_1Y . When the composition of the liquid phase reaches Y then the solution will also be saturated with respect to potassium chloride, and sucrose can no longer be crystallised in the pure form. If the composition of the original solution had been represented at P_2 then as the result of evaporation it would change along the line P_2Q_2 . On reaching Q_2 crystallisation would commence, but this time it would be potassium chloride which would crystallise and not sucrose.

If we replaced potassium chloride with a hypothetical substance (T) which would form a hydrated double compound with sucrose (say $C_{12}H_{22}O_{11} \cdot T \cdot 2H_2O$), and if this substance had a similar solubility and molecular weight to potassium chloride we would expect to obtain a phase equilibrium diagram similar to that shown in Fig. 2/13.

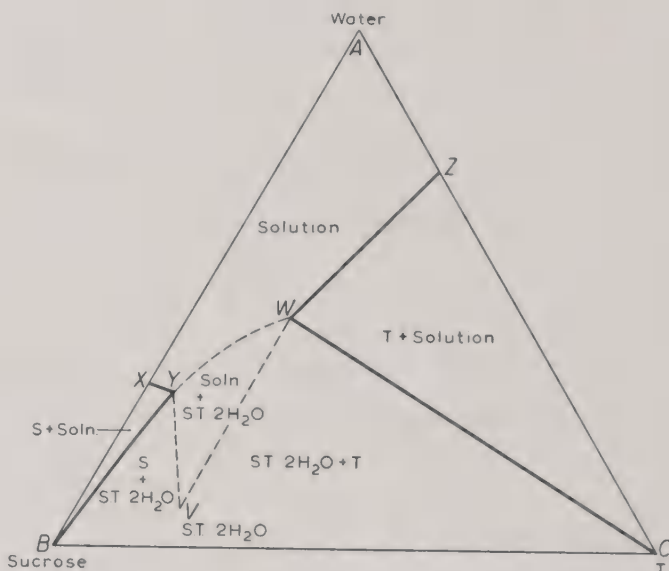


Fig. 2/13. Effect of compound formation on equilibrium relationships.

In this case the composition of the double compound would be represented by point V and there would be two ternary points Y and W , and Y would be at a rather higher 'purity' with respect to sucrose than in the case illustrated in Fig. 2/12. Thus double compound formation would result in the cessation of crystallisation of sucrose in its pure form at an earlier stage than if double compound formation were absent, but this is not related to salting-in or salting-out behaviour which PRINSEN-GEERLIGS²² considered an important criterion of double compound formation. The purity at the ternary point with respect to one of the solutes does, however, vary consistently with change in solubility of the second solute³³. Thus if the solubility of the second solute is higher, then point Z will be closer to the corner C in Fig. 2/13 and the proportion of C to B at point Y will be increased *i.e.* the purity will be lower with respect to solute B (in this case sucrose). An example of this is illustrated in Fig. 2/16d in the system water - sucrose - fructose, where fructose is a solute of high solubility. On the other hand, if solute C has a low solubility then the solution will soon be saturated with respect to this substance when evaporation is

The triangular diagram has certain limitations when dealing with solubility characteristics in a system containing a solute of very low solubility and one of reasonably high solubility. Such conditions are of frequent interest in sugar boiling when syrups become saturated with respect to calcium sulphate and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystallises²¹. In Fig. 2/14 is illustrated a convenient means for representing the system water – sucrose – calcium sulphate, using solubility figures for CaSO_4 in sucrose solution determined by STOLLE⁵³. The use of this type of diagram as an extension of the JÄNECKE principle has been described by KELLY⁵⁴ for this particular system.

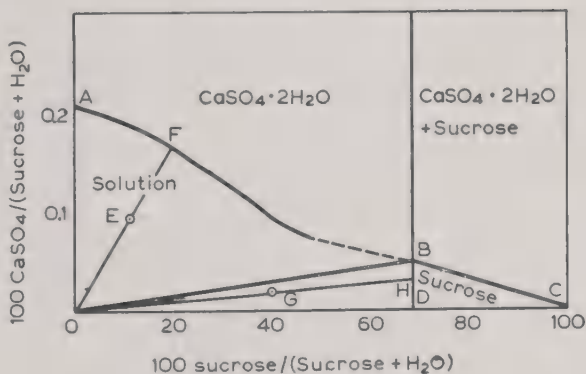


Fig. 2/14. System CaSO_4 -sucrose- H_2O ; *J. Chem. Educ.* 31 (1954) 637.

Solution of composition E would, on evaporation, change in composition along line EF in a direction away from O or point representing pure water. At point F , crystallisation of gypsum will commence, and composition of liquid phase will change along the line FB . At point B sucrose will also crystallise and a mixture of sucrose plus 640 p.p.m. of CaSO_4 as the dihydrate will continue to crystallise until evaporation is complete. Only solutions with a composition below the line OB will allow any sucrose free from gypsum to crystallise. For example, a solution with composition represented by point G would, on evaporation, change composition along

line GH . At point H sucrose free from CaSO_4 would crystallise and continue to do so with the composition of the liquid phase changing from H to B when gypsum begins to crystallise. This diagram gives an indication of the difficulty of obtaining pure sucrose by crystallisation if a second solute of low solubility is present. No amount of washing during the centrifuging process will improve the purity of the sucrose unless a higher purity of molasses is tolerated. There may appear to be a temporary improvement, but if the process is continued long enough equilibrium will soon be reached and double crystallisation continue. In these circumstances it is necessary to remove the solute of low solubility by some means other than crystallisation, *e.g.* adsorption, and this of course is done in refinery practice. Similar comment might be made when saturating conditions are obtained with solutes of higher solubility such as potassium sulphate or potassium chloride. It is necessary to remove these substances by ion exchange or other suitable techniques if the maximum benefit is to be obtained from sucrose crystallisation.

As has already been mentioned crystallisation of sucrose associated with change of temperature is also of considerable technical importance. For these conditions a polythermal diagram is required. Unfortunately no three component systems have been worked out completely over the full range of temperatures, but sufficient is known of some of the two-component systems to get a first approximation of the conditions to be expected in a three component system. This is done for the system which is believed to be

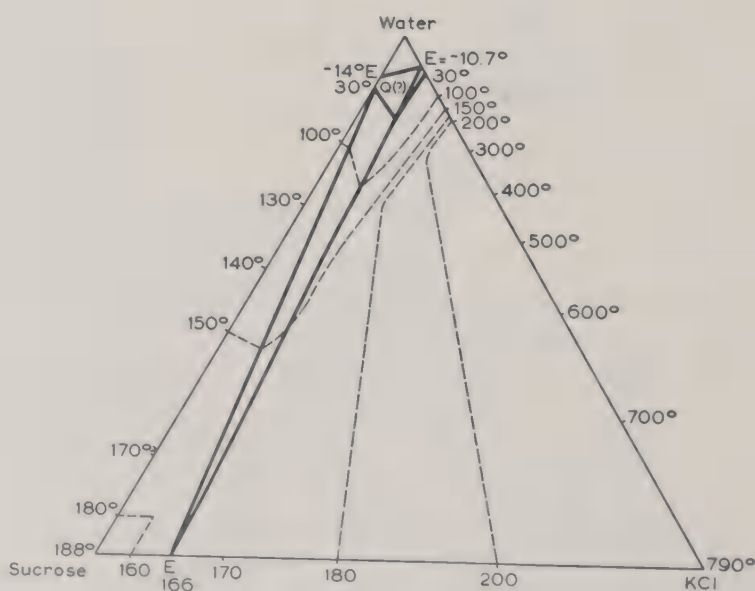


Fig. 2/15. Polythermal phase equilibrium diagram.

the simplest *viz.* water – sucrose – potassium chloride. The substitution of fructose as the third component might have some advantages from the point of view of the discussion, but rather less is known of the two component systems in this case and the diagram used is preferred for the time being. This is shown in Fig. 2/15. Whereas in previous phase equilibrium diagrams the proportions of the respective components have been given on the basis of weight percentages, for the polythermal diagram molar proportions are used as these are considered to spread the high temperature conditions rather better.

The solubility of potassium chloride in water is recorded⁵⁵ from -2.24° to 454° C, with a eutectic at -10.72° C at 0.057 mole fraction of potassium chloride. Eutectics of this type, involving water and a solution are often referred to as cryohydric conditions. With sucrose having a melting point of 188° C and potassium chloride 790° C a eutectic may be expected with a relatively high mole fraction of sucrose and a temperature perhaps 20° C below the melting point of sucrose. Some mixed melting point tests made by KELLY⁵⁶ indicated a eutectic at 0.876 mole fraction of sucrose and a temperature of 166° C. The probable isotherms for Fig. 2/16 were plotted from these data. If we had built a space model then the isotherms would be contour lines on the surface of a vertical prism, with a 'valley' generally relating the three binary eutectics and a ternary eutectic – or quaternary point of the system being located somewhere near the low temperature binary eutectics. VAN DER LINDEN³⁹ gave special consideration to relationships between eutectic conditions and the formation of molasses.

From information which is now available it may be said that the eutectic coinciding with the invariant point of the system is probably at a much lower concentration of total solids than that normally experienced with molasses. However, if the molasses is saturated with respect to a solute other than sucrose then the composition will be at a ternary point of a three component system for a particular temperature. By changing the temperature the relative temperature coefficients of the solubility of the two solutes may result in a further yield of pure sucrose, but within the temperature range available for practical purposes advantages to be gained from a change in processing will be very limited indeed from this point of view. There may, however, be other benefits to be gained from a change in operating temperature.

It is possible to 'break-down' molasses into a number of three component systems and to consider phase equilibrium conditions in these systems individually. In Fig. 2/16 are recorded six of these diagrams^{3, 20, 24, 56} which contain as their third component one of the constituents of molasses.

In Figs. 2/12 and 2/14 are two other systems which could quite well be associated with those in Fig. 2/16.

Figure	System
2/16a	water-sucrose-NaCl
2/16b	water-sucrose- K_2SO_4
2/16c	water-sucrose-glucose
2/16d	water-sucrose-fructose
2/16e	water-sucrose-raffinose
2/16f	water-fructose-glucose

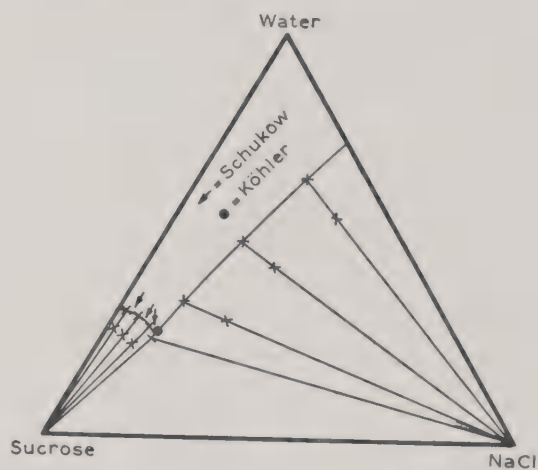


Fig. 2/16a. System water-sucrose-NaCl at 30° C; *J. Appl. Chem. London* 4 (1954) 401.

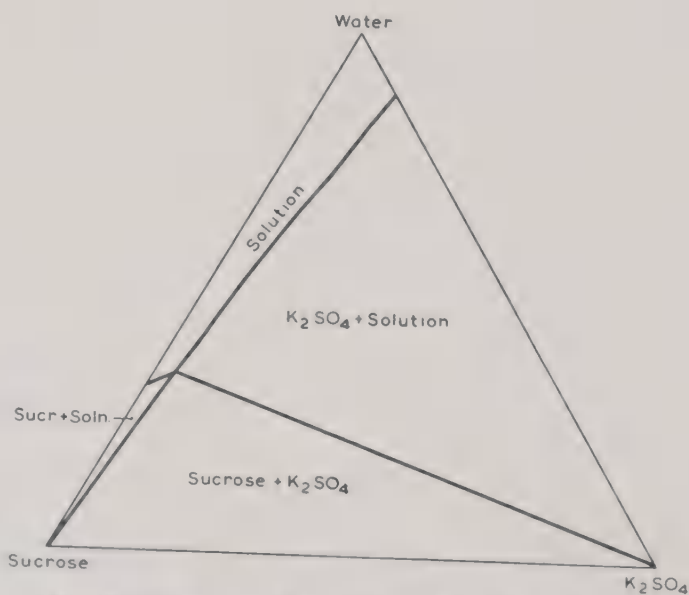


Fig. 2/16b. System water-sucrose- K_2SO_4 at 30° C.

There is also now available information at 30° C concerning the phase equilibrium conditions of several four component systems which are of interest when studying molasses. The graphical delineation of a four component system presents certain difficulties by way of geometry. Some workers prefer perspective views of space models, and others various projections of surfaces within these models. Here it is preferred to use the basal projection of a vertical triangular prism, with the three solute components represented at the corners of the triangle and the solvent expressed as units/100 units of total solute. The shape of the surface of the prism can be represented by contour lines of equal solvent concentration and in this case as the solvent is water, may be referred to as isohydrores⁵⁴.

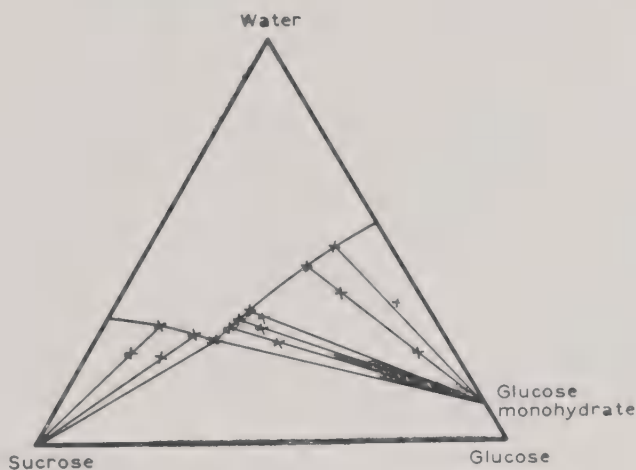


Fig. 2/16c. System water-sucrose-glucose at 30° C; *J. Appl. Chem. London* 4 (1954) 405.

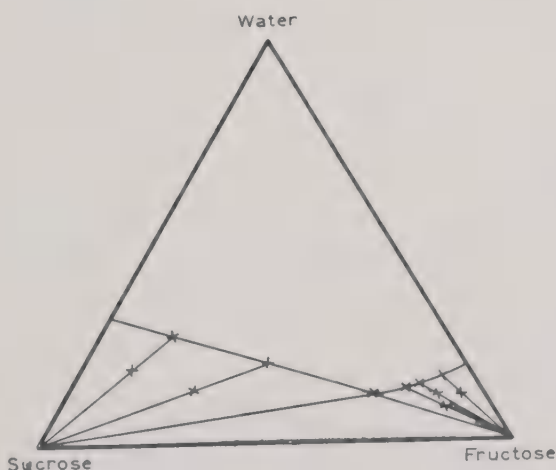


Fig. 2/16d. System water-sucrose-fructose at 30° C; *J. Appl. Chem. London* 4 (1954) 405.

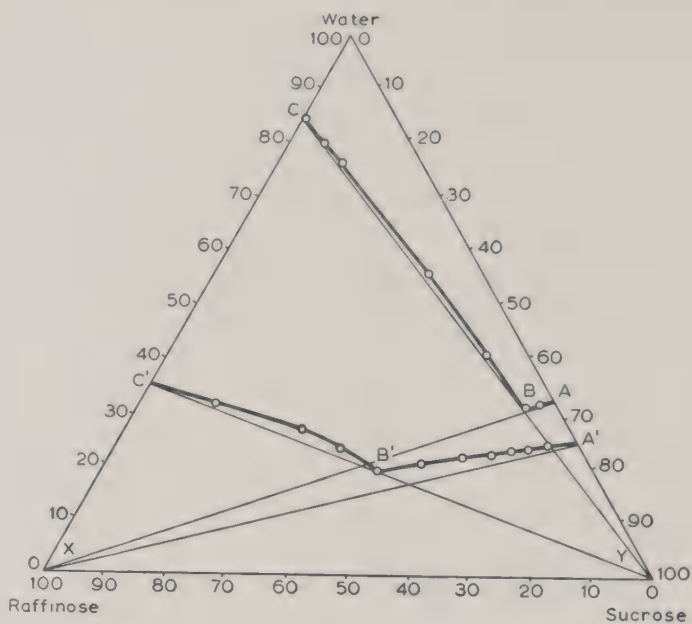


Fig. 2/16e. System sucrose-raffinose-water at 25° C and 64° C; *Ann. Chim., Rome* 44 (1954) 797.

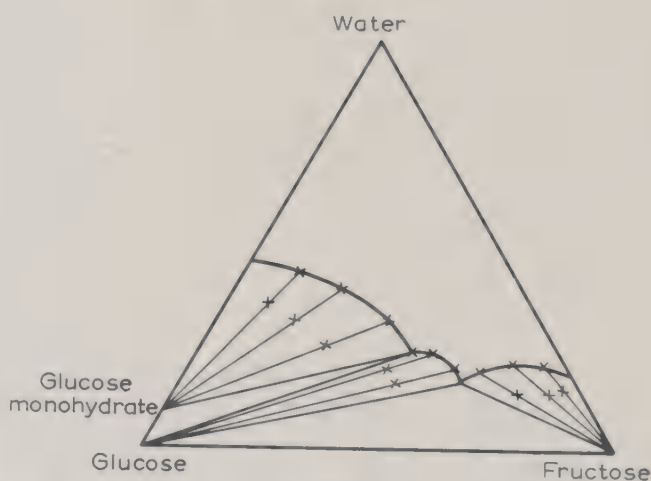


Fig. 2/16f. System water-glucose-fructose at 30° C; *J. Appl. Chem. London* 4 (1954) 409.

In Fig. 2/17 are recorded four of these diagrams^{24, 25, 57}. In (a), (c) and (d) it is interesting to note the influence of the hydration of glucose. Al-

Figure	System
2/17a	water-sucrose-KCl-glucose
2/17b	water-sucrose-KCl-fructose
2/17c	water-sucrose-glucose-fructose
2/17d	water-KCl-glucose-fructose

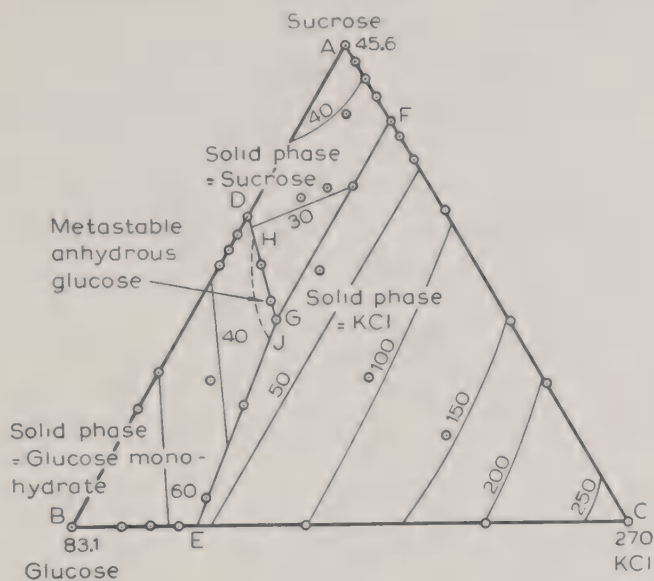


Fig. 2/17a. Equilibrium-phase relationships for the quaternary system sucrose-glucose-KCl-water; *J. Appl. Chem. London* 5 (1955) 69.

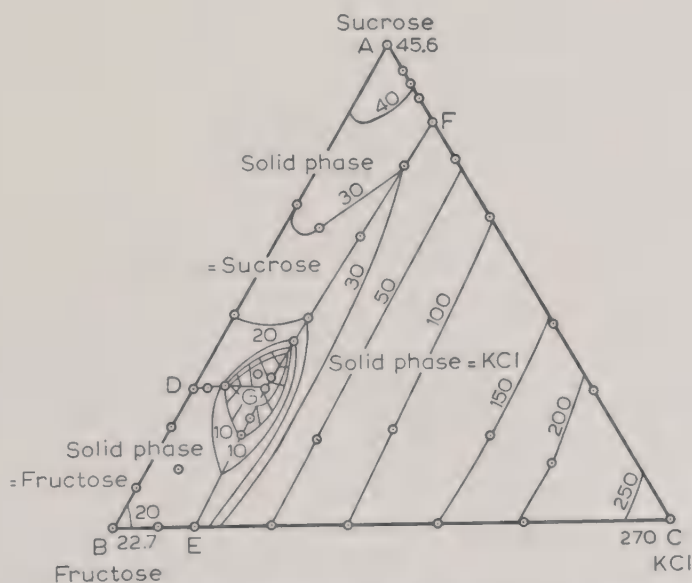


Fig. 2/17b. Equilibrium-phase relationships for the quaternary system sucrose-fructose-KCl-water; *J. Appl. Chem. London* 5 (1955) 66.

though glucose normally crystallises as the monohydrate at a temperature of 30°C , the anhydrous form can be a stable phase in the presence of solution containing fructose. This was also observed in the three component system of water – glucose – fructose as shown in Fig. 2/16f.

When considering sugar cane molasses, diagram (c) of Fig. 2/17 will

probably be the most useful of the four component systems. Owing to the lower solubility of glucose than fructose the molasses would become saturated with respect to glucose before fructose if the two reducing sugars

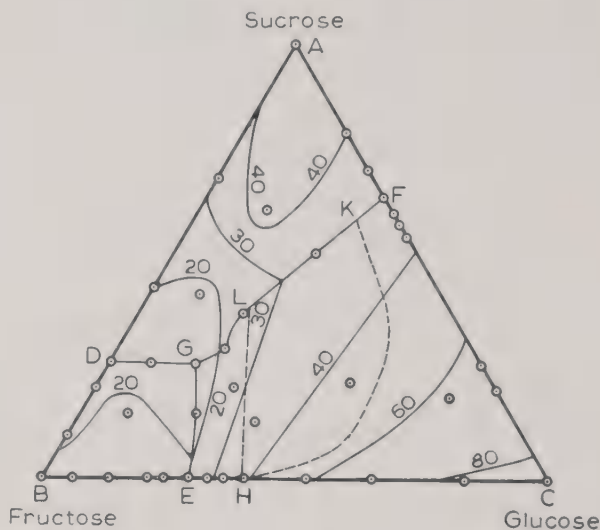


Fig. 2/17c. Equilibrium-phase relationships at 30° C for the system sucrose-fructose-glucose-water; *J. Appl. Chem. London* 5 (1955) 120.

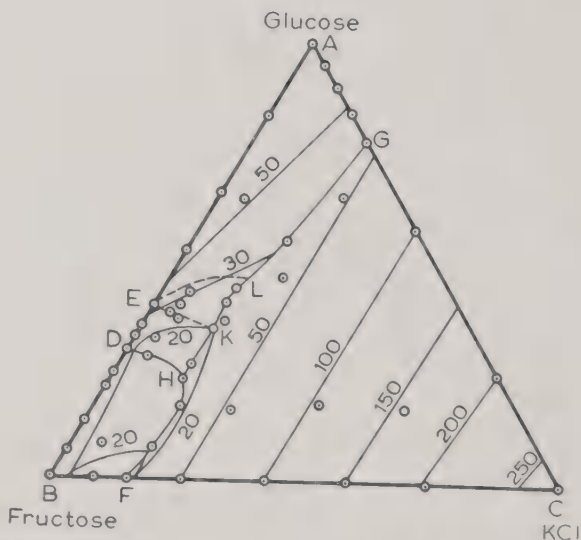


Fig. 2/17d. Equilibrium-phase relationships at 30° C for the system glucose-fructose-KCl-water; *J. Appl. Chem. London* 5 (1955) 123.

are present in equal proportions. This would appear to be the case for the 'average' Louisiana molasses the composition of which is quoted in detail by SPENCER and MEADE⁵⁸. There are, however, indications that the two reducing sugars are not always present in equal proportions and an excess

of fructose has been reported from some samples of Queensland molasses⁵⁹ which could occasionally be sufficient for this to be controlling rather than glucose. Studies in Java indicated conditions of this type to be more usually associated with immaturity of cane.

Diagram (a) or (b) of Fig. 2/17 would be the most suitable for the study of a molasses of the type reported from Hawaii in which crystalline potassium chloride has been recognised together with sucrose⁴³.

In order to complete the information which is at present available by way of phase equilibrium diagrams of the systems containing sucrose, one set of conditions for the five component system water – sucrose – glucose – fructose – potassium chloride²⁶ is illustrated in Fig. 2/18.

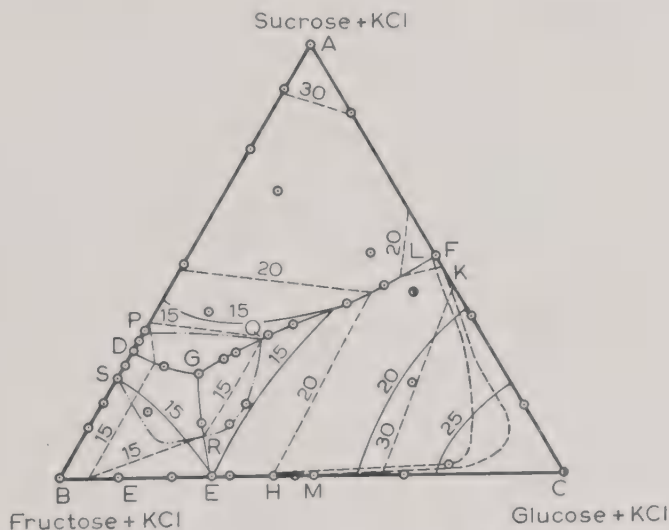


Fig. 2/18. Equilibrium-phase relationships at 30° C for the system sucrose-fructose-glucose-KCl-water. — = Solutions saturated with three solutes; - - - = Isohydrores; ··· = Potassium chloride isopleths; — · — = Solutions of highest solute concentration. *J. Appl. Chem. London* 5 (1955) 170.

This diagram indicates conditions when the solution is saturated with respect to potassium chloride and one other solute. The diagram is in effect a double basal projection of a triangular prism with two surfaces, one surface representing the variations in solvent concentration according to the height of the ordinate, and the other surface representing the variations in the concentration of potassium chloride.

When considering the composition of molasses in relation to phase equilibrium conditions the concentration of specific impurities relative to the water content should be examined. If the specific impurity-water ratio is similar to or greater than the value for a solution saturated with this

impurity in water at the temperature conditions of interest, then no further sucrose may be crystallised from the molasses unless the impurity also crystallises. The impurities likely to be of main interest from this point of view are glucose, potassium chloride and potassium sulphate. If the impurity-water ratio is significantly less than for the solubility of the pure substance then it may be concluded either that more sucrose will crystallise if given the opportunity or some other substance is preventing crystallisation. KELLY⁵⁷ has studied molasses in this manner and prepared synthetic solutions containing sucrose, fructose, glucose and potassium chloride in proportions experienced in the molasses itself. These synthetic molasses mixtures have shown quite clearly in the majority of cases that the composition does not approach conditions of saturation with respect to fructose, glucose or potassium chloride. In these circumstances sucrose will continue to crystallise quite readily, and as might be expected from reference to the appropriate phase equilibrium diagram. It is evident that double salt formation at least between one or other of these three particular solutes and sucrose is not a factor in restricting sucrose crystallisation. Additions to the synthetic system of a further single component of a type experienced in molasses have been tried and it was found that aspartic acid, for example, has quite a definite inhibiting influence on the crystallisation of sucrose. The possibility of other substances or combinations thereof behaving in a similar manner could be readily examined in this way.

7. Ternary Systems with Two Liquid Phase Solutes

The solubility of sucrose has been determined in several systems which are mixtures in varying proportions of water and an organic liquid solvent which is miscible with water. HIRSCHMÜLLER has recorded the solubility of

TABLE 4
SOLUBILITY OF SUCROSE IN AQUEOUS ETHANOL*

Alcohol in vol. %	Sucrose in g/per 100 ml of solution		
	25° C	30° C	35° C
20	78.5	89.26	93.0
35	62.8	77.05	81.38
50	52.8	60.25	64.50
65	31.5	35.79	41.17
80	9.3	16.26	23.92
95		0.17	0.76

* See Table 26 in P. HONIG, *Principles of Sugar Technology*, Vol. I, Elsevier Publishing Co., Amsterdam, 1953.

sucrose in mixtures of water and ethyl alcohol. These values were obtained by SCHREFELD⁶⁰ at 14° C. More recently information on this system has been extended by REBER⁶¹ at 25° C and ROSSI⁶² at 30° and 35° C. Values from the results of REBER and ROSSI are recorded in Table 4.

In Table 5 are solubility values at 25° C for sucrose in aqueous solutions of glycerol and propylene glycol. These results were published by FEY, WEIL and SEGUR⁶³.

TABLE 5
SOLUBILITY OF SUCROSE IN AQUEOUS GLYCEROL AND PROPYLENE GLYCOL AT 25° C

% Glycerol in solvent	Sucrose in solution % by weight	% Glycol in solvent	Sucrose in solution % by weight
0	67.89	0	67.89
25	59.4	25	58.8
50	44.8	50	42.7
75	25.4	62	33.5
82.5	20.0	75	21.8
95	9.9	95	4.5
99.96	5.7	99	1.9

It would appear that sucrose is slightly soluble in glycerol itself and to a lesser extent in propylene glycol. It is for all practical purposes insoluble in anhydrous ethanol and also in such solvents as benzene.

Advantage is taken of the low solubility of sucrose in aqueous ethanol solutions to prepare sucrose of high purity by virtually effecting precipitation. As the particle size of sucrose precipitated in this manner is extremely small it has found some application as seed crystal during the graining process of sugar boiling⁶⁴.

Aqueous glycerol and propylene glycol solutions are mainly of interest for pharmaceutical preparations. However, because of the high viscosity of glycerol it is useful as a medium for the dispersion of sucrose crystals when making microscopic observations.

Any one of these solutions may be used at suitable concentrations for the removal of crystal sucrose from aqueous mother liquors, but care must be exercised in developing a technique suited to the particular circumstances.

The solubility of sucrose in aqueous acetone solutions at 30° C has been studied by VERHAAR⁶⁵. He has shown that at this temperature two liquid phases can exist in equilibrium over the concentration range intermediate between aqueous solutions containing up to 36.5 parts of acetone/hundred of solvent and acetone solutions containing up to 20.6 parts of water/hundred of solvent (Fig. 2/19). HERZ and KOCH⁶⁶ had previously observed somewhat similar behaviour in their study of the system at 25° C.

For solutions of sucrose in methanol there seems to be only data recorded toward the end of last century. SCHEIBLER⁶⁷ gives 3.43 and 0.44 g sucrose/100 ml for solubility of sucrose in 83.5 % and 92.5 % methanol respectively. LINDET⁶⁸ found the solubility in pure methanol to be 0.49 g/100 ml although no temperature is recorded.

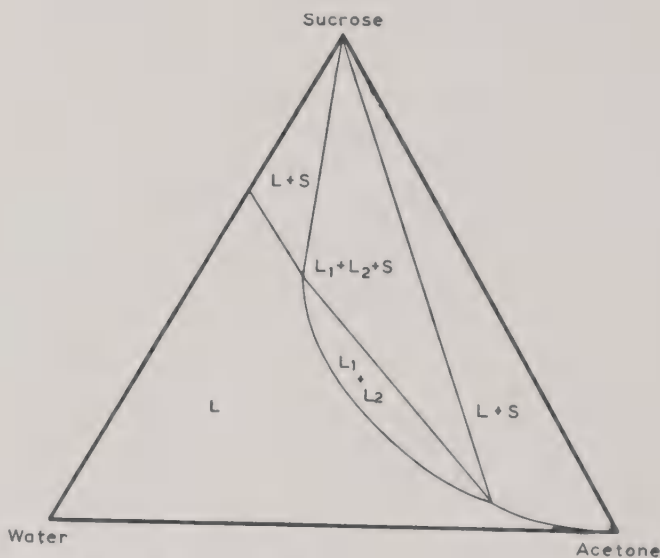


Fig. 2/19. Phase-equilibrium diagram at 30° C for sucrose-water-acetone (VERHAAR).

LOBRY DE BRUYN⁶⁹ records a much higher value with 100 parts of methanol dissolving 1.18 parts of sucrose at 19° C. The values of LINDET⁶⁸ are approximately in agreement with those of GUNNING⁷⁰ who found at 15° C only 0.3 g sucrose to dissolve in 100 ml of pure methanol. At the same temperature he found 3.8 g sucrose to dissolve in 100 ml of 80 % methanol, falling to 0.60 and 0.45 for 90 % and 95 % methanol respectively. HOLTY⁷¹ reported sucrose to be soluble in pyridine to the extent of 6.45 g/100 g of solution at 26° C.

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CHAPTER 3

NUCLEATION IN SUPERSATURATED SUCROSE SOLUTIONS

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1. Introduction

The rate of adjustment of a metastable, homogeneous melt or solution is prescribed by the consecutive acts of nuclei formation and growth. The procreating nuclei (a) may already exist latently in the undercooled melt or undersaturated solution and merely require activation by cooling below the transition point; (b) may be generated spontaneously as the equilibrium point is exceeded; (c) may consist of fortuitous contaminating particles; or (d) may be substances added as seeds which stimulate the change to the stable configuration of the system. The first possibility explains many of the anomalous and peculiar effects of history and treatment of the sample on the rate of phase transition. Most nucleation theories to date regard the spontaneous adjustment of supercooled systems as being essentially homogeneous in nature, as exemplifying (b); although the quantitative significance of variations (a) and (c) have been considered¹. Such considerations suggest that nucleation by process (c) entails more than the mere presence of the potentially effective foreign particle^{2, 3a}. Treatment (d) almost invariably leads to prompt and complete equilibration of the initially metastable system, although BUNN⁴ has suggested the intriguing possibility that a perfect crystal may not grow at all when placed in appropriate nutrient solution. Dislocations or imperfections would be necessary to initiate growth. Of course, these are ever present in real crystals.

The current trend in sugar boiling practice is definitely toward the use of full seeding methods for graining. There are tantamount to case (d) above; which immediately suggests that for practical purposes nucleation considerations may be circumvented. However, this trend is by no means completely consummated, and methods of 'boiling to grain' and 'shock seeding' are still emphasized in various sugar houses. These invoke the

operation of factor (a), (b) and (c) of the above classification. In some respects growth is also merely the extension of nucleation, and most modern theories of crystal growth require some form of nucleation, even upon an established base of crystallizing material.

The importance of the mechanism of nucleation is therefore doubly emphasized, and the following discussion will consider the adjustment of supersaturated sugar solutions in terms of both this initiating step and the subsequent growth.

2. General. Nucleation and Growth

The commonness of supercooling, supersaturation, and metastable phenomena in general is apparent from such ordinary examples as the failure of many melts to solidify upon cooling, the occasional 'sugaring' of honey and molasses, etc. Water may be cooled rather readily several degrees below its freezing point without solidifying⁵. Numerous cases have been reported when even large lakes have supercooled appreciably. Ordinary glycerine has a melting point of 18°C , yet it rarely solidifies in the wintertime when temperatures far below this point prevail.

Experience indicates that many of these suspended states adjust themselves to the proper condition once the change is instigated by a proper stimulus or disturbance. However, there are exceptions to this generalization. Witness the case of glass – believed by many to be a supercooled liquid, yet in which vitrification proceeds very, very slowly even when seeded.

TAMMANN⁶ described much of the above in a phenomenological way by means of his rate of nucleation (K.Z.) and crystallization velocity (K.G.) curves. Both these curves exhibit maxima with respect to increasing supercooling – the former (K.Z.) being much sharper than the latter (K.G.)

The intercept in Fig. 3/1 expresses the well known tendency of unseeded

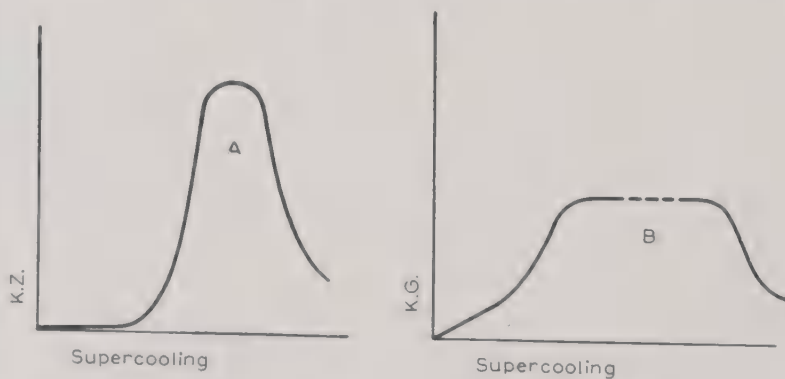


Fig. 3/1. TAMMANN curves. A: nucleation number, B: growth rate.

melts and solutions to supercool and supersaturate, respectively, a definite extent before crystallization sets in. This period, in the case of solutions, is the 'metastable limit' or 'supersolubility' of OSTWALD⁷. MIERS⁸ was able to express these values quite definitely for a number of substances as illustrated in Fig. 3/2. Within the metastable region of Fig. 3/2 a crystal seed will grow but none will form spontaneously from clear and quiescent solution or melt. However, beyond the supersolubility point crystals will form spontaneously and, of course, proceed to grow. The time limit implied in these distinctions is more or less indefinite, and most workers in the field regard the supersolubility concept as being only qualitative. It is, nonetheless, very practical.

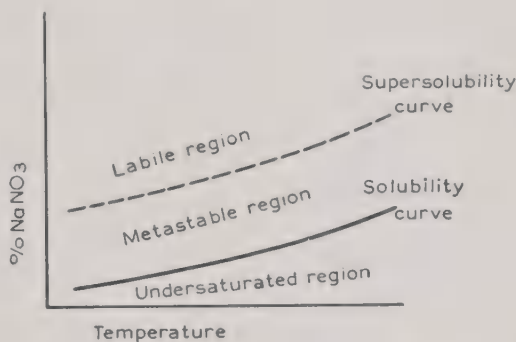


Fig. 3/2. OSTWALD's supersolubility concept.

One does not have to seek far for an explanation of the supersolubility limit. The increased vapor pressure of small droplets, and hence the enhanced solubility of fine particles, is an established even though transitory reality. A nucleus formed in the metastable region is extremely small at the inception and will dissolve or melt rather than grow on account of the increased solution potential associated with its small size. As the metastability increases, the size of the incipient crystal which can be tolerated by the solution decreases to a critical size where growth rather than dissolution prevails. This idea is elaborated in most modern theories of the nucleation process.

In essence: The GIBBS-THOMSON equation stipulates the following variation of solubility with particle size:

$$\ln \frac{P}{P_{\infty}} = \ln \frac{L}{L_{\infty}} = \frac{2 \sigma M}{dRT r}$$

$$r^* = \frac{2 \sigma M}{dRT \ln(L/L_{\infty})}$$

Here P and L are the vapor pressure and solubility respectively of the particle of radius r , and the corresponding ordinary values are those of a plane surface of $r = \infty$. σ is the interfacial tension, d the density of the separating phase, and M its molecular weight. As usual, R is the gas constant and T the temperature. Now, it is sound kinetics to write

$$K.Z. = B \cdot \exp \left(- \frac{E_{\text{Act.}}}{RT} \right)$$

for the velocity of nucleation, $K.Z.$ B is a constant of proportionality which is evaluable by modern theory. The energy of activation of the nucleation process, $E_{\text{Act.}}$, would, as a minimum, be the work required to form the critical nucleus, r^* . If this is taken to be a sphere

$$E_{\text{Act.}} = \frac{4}{3} \pi r^{*2} \sigma = \frac{16 \pi M^2 \sigma^3}{3 d^2 R^2 T^2 \ln^2 S}$$

This equation, which suggests that the work of nucleation is one-third the work of forming the surface of the nucleus, follows from the following considerations. The relation between the surface tension and the pressure difference across a curved surface may be developed by considering the transfer of an infinitesimal amount of the liquid entirely into surface. The net work done is equal to the product of the pressure difference within and without the curved surface, Δp , and the volume transferred. This energy must equal that gained as surface free energy, $v i \sigma$;

$$(\Delta p) dv = \sigma dA$$

Now, for a sphere

$$v = \frac{4}{3} \pi r^3 \text{ and } A = 4 \pi r^2$$

$$dv = 4 \pi r^2 dr \text{ and } dA = 8 \pi r dr$$

Since

$$dv/dA = r/2 \text{ and } v = \frac{1}{3} r A$$

it follows that

$$\Delta p = \frac{2\sigma}{r}$$

The work of forming a nucleus is the net work of forming the surface and that needed to form the bulks of the particle; namely

$$W = W_s - W_v = \sigma A - (\Delta p)v = \sigma A - \frac{2\sigma}{r} \cdot \frac{rA}{3} = \frac{1}{3} \sigma A = \frac{1}{3} W_s$$

where S , the supersaturation, is written for P/p_∞ or L/L_∞ . It then follows that

$$K.Z. = B \cdot \exp \left(- \frac{16 \pi M^2 \sigma^3}{3 d^2 R^2 T^2 \ln^2 S} \right)$$

The curve representing this equation is a very steep one, and the first part of Fig. 3/1^A reproduces it very well. The maximum and subsequent

parts of the curves in Fig. 3/1 are probably due to the tremendous increase in viscosity as supercooling or supersaturation increase. The falling-off may be reproduced by adding a proper term for this effect, $\exp\left(-\frac{E_{vis}}{RT}\right)$, to the work expression⁹. This expression is confirmed by a wide variety of experiments⁴ and accounts fairly well for the behavior of sugar solutions. The VOLMER theory was first applied to this particular case by CASSEL and LANDT¹⁰. These considerations will be discussed in detail in the next section.

The basic KELVIN equation has only recently been substantiated in an irrevocable way by LAMER¹¹. VANHOOK has also recently demonstrated its reality in sugar solutions¹². For this purpose very fine sugar powder was added to solutions which had previously been saturated with ordinary crystals. The transitory enhanced solubility of the fine crystals occasioned an immediate rise in the concentration, which soon subsided to the normal level as this excess crystallized on the larger particles (Fig. 3/3).

The theory just outlined concurs with the general observation that homogeneous nucleation is generally a more difficult matter than subsequent growth. Other features of the nucleation process, but by no means all, are

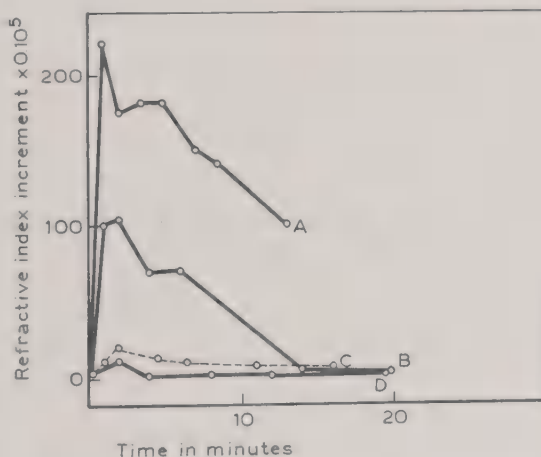


Fig. 3/3. Change in the refractive index upon mixing excess sucrose crystals with previously saturated solution. A: 30% by weight of fine crystals, B: 10% by weight of fine crystals, C: 30% by weight of coarse crystals, D: 10% by weight of coarse crystals. See ref. ¹².

also explicable by this theory or its corollaries. For instance; a maximum supercooling of 20–30° C, or an equivalent supersaturation, is quite common, and this is just about the right order of magnitude according to theoretical estimates. It is also common knowledge that stirring, mechanical shock, or various radiations augment nucleation. For example, most directions

for the quantitative precipitation of MgNH_4PO_4 suggest that the sides of the container be scratched with a glass rod in order to induce crystallization. It is also rather easy to prepare highly supersaturated solutions of ordinary hypo, unless the solution is stirred. Likewise, it is possible to induce crystal formation in many substances that supercool readily by irradiation with sonic or supersonic irradiation, electromagnetic vibrations, electrostatic discharges, X-ray, etc. These agents are probably effective on account of their strong orienting influence; which acts to supplement and reinforce the fluctuations required to form a critical nucleus.

If a melt or solution is filtered before supercooling it is frequently less prone to nucleate than when unclarified. This suggests the common occurrence and strong influence of foreign nucleating particles such as dust, etc. Similarly, crystals form in the bottom portions of a sample and on the surface of the container. This may be due to the settling of a foreign particle, the effect of gravity, or possibly the influence of surface tension forces. If a substance is just melted before supercooling it is likely that it will sustain less supercooling than if the melting point had been exceeded by $20\text{--}30^\circ\text{C}$; or, repeated melting will also frequently increase the resistance to supercooling. This behavior has been ascribed by some early workers to the 'memory capacity' of the substance. The further from the transition point the treatment, the more the system 'forgets' the former stable configuration and becomes less apt to resume that state. It seems obvious that this behavior is either one of deactivation of foreign nuclei or the destruction of the order-disorder which surrounds the transition point.

Another common habit of liquids is that of supercooling to a greater extent in small samples than in large quantities. A few of TURNBULL'S¹³ figures illustrate this behavior (Table 1).

TABLE 1
SUPERCOOLING AND SIZE OF SAMPLE¹³

	Maximum supercooling, $^\circ\text{C}$	
	large sample	small sample
Hg	14	46
water	36.8	39
Ga	55	76
Sn	31	110
Bi	30	90

Here again it appears that the nucleation observed in macro-samples is more often than not induced by extraneous seeds. When the sample is separated

into smaller ones these foreign inoculants are isolated and the effect of true homogeneous nucleation is developed.

It is often observed that minute amounts of impurities exert profound effects on the starting and growth of many crystals. Thus, even a trace of Pb^{++} ion promotes the growth from solution of transparent cubes of ordinary salt in place of the transcluculent or opaque crystals usually obtained. WALKER¹⁴ of the Bell Telephone Laboratories has observed a similar improvement in quartz crystals when grown above the critical conditions from alkaline solutions containing small amounts of sodium oleate. SUZUKI¹⁵ claims similar benefits upon the addition of minute amounts of Mn and Co ions in sugar crystallization. These 'mineralizing' effects may be the result of differential adsorption of the impurity on the nucleus or growing crystal, or may be a manifestation of the strong influence of the σ^3 term suggested by the above thermodynamic theory. The exact mechanism has not been worked out yet, and the explanation awaits theoretical understanding and practical exploitation.

3. Nucleation Theory as Applied to Sugar Solutions

(a) *Supersolubility*

Large and unsymmetrical molecules are liable to undergo undercooling or supersaturation under ordinary circumstances while small and uniform molecules exhibit relatively little or no tendency to enter these metastable states¹⁶. The behavior of a system in a metastable condition may be described effectively by means of the OSTWALD supersolubility curve. Fig. 3/4 rep-

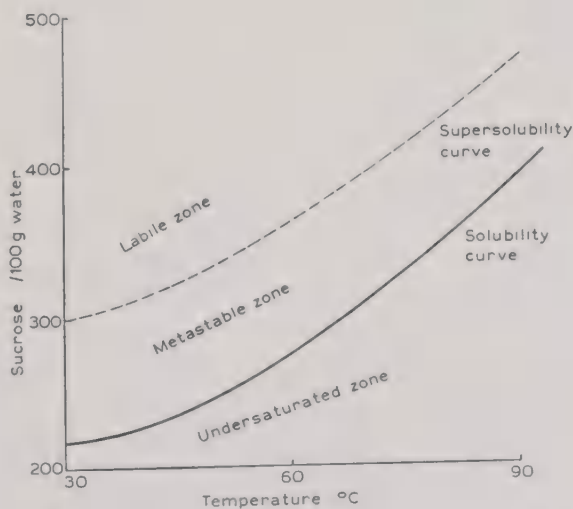


Fig. 3/4. Approximate supersolubility diagram for sucrose.

in boiling conditions if the grain had been formed by either waiting or shocking, and is probably the reason for less certain and uniform results in these cases.

The supersolubility curve cannot be regarded as representing a critical threshold condition, since it is frequently observed that solutions crystallize at oversaturations considerably less than $S = 1.3$, and still more concentrated syrups are often stable for indefinite periods^{18, 19}. The former occurrence is usually the result of accidental inoculation with a fragment of crystal or dust particle or by some kind of shock^{18, 19}. The latter case of stability up to supersaturations of 1.5–1.6 can be realized only by very careful preparation of syrups under virtually aseptic conditions, and storage in hermetically sealed containers. The Figs. 3/6 and 3/7 illustrate the nucleat-

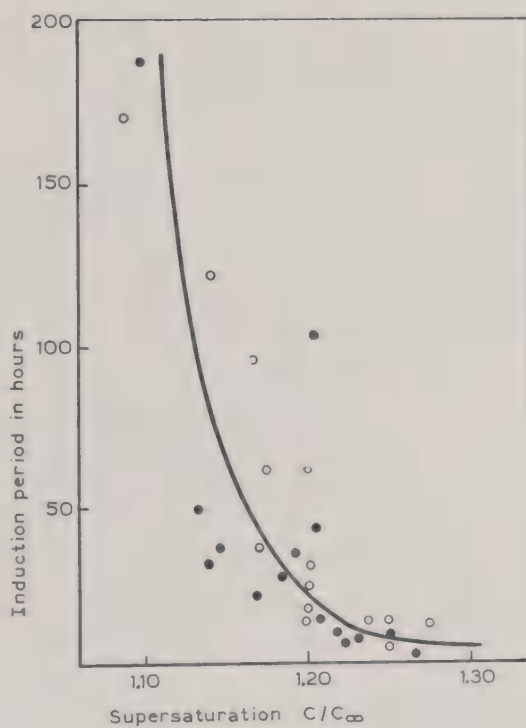


Fig. 3/6. Nucleation rate of sucrose solutions at 25° C (DUNNING and SHIPMAN^{3b}).

ing behavior of such carefully prepared solutions. The first of these two figures suggests that the onset of crystallization becomes apparent above a supersaturation of about 1.3, when only several hours is taken as a convenient period of observation. The second figure demonstrates that the establishment of visible centers of growth is catastrophic above $S \approx 1.5$.

The law of mass action indicates that the concentration of critical nuclei will be $c^* = K c^n$ for this equilibrium state. The equilibrium constant K may also be expressed in terms of the equivalent free energy

$$-\Delta G = kT \ln K$$

The free energy involved in forming the nucleus must be regarded with respect to the normal or bulk free energy of the crystallizing phase; in which case it is nothing but the surface free energy of the nucleus. This amounts to σA , where A is the surface area of the nucleus and σ its interfacial tension. The concentration must likewise be expressed with respect to the crystallizing phase or $\frac{c}{c_\infty}$. This is the ordinary degree of supersaturation in usual units. The concentration of critical nuclei then becomes

$$C^* = \left(\frac{c}{c_\infty} \right)^n \cdot \exp \left(\frac{-\sigma A}{kT} \right)$$

The critical nucleus represents a maximum in the free energy-size relationship, and stability will be occasioned by any reduction in this particular value. This may be realized either by loss of molecules, which is tantamount to dissolution, or by addition of molecules, which is equivalent to growth. If g is the probability per unit time that the critical nucleus will follow the latter path then $g c^*$ is nothing but the nucleation rate J . The resulting equation

$$J = g \left(\frac{c}{c_\infty} \right)^n \cdot \exp \left(\frac{-\sigma A}{kT} \right)$$

has the familiar form of the general rate formula, where, however, the individual terms have explicit significance. It remains to express A as a function of temperature and concentration.

The surface of the critical nucleus is $A = 4\pi r^{*2}$, or $A = \frac{16\pi \sigma^2 m^2}{d^2 \left(kT \ln \frac{c}{c_\infty} \right)^2}$

when combined with the GIBBS-THOMSON equation. In this form m/d is the volume of a molecule in terms of its mass and density. The number of molecules in the critical nucleus is given by $n = \frac{4\pi r^{*3} d}{3m}$. The GIBBS-

THOMSON equation also gives $\left(\frac{c}{c_\infty} \right)^n = \exp \left(\frac{2n\sigma m}{dr^*} \cdot \frac{1}{kT} \right)$. If these values are

substituted in the rate equation, the result is

$$J = g \cdot \exp \left(- \frac{16 \pi M^2 N \sigma^3}{3 d^2 R^3 T^3 \left(\frac{\ln c}{c_\infty} \right)^2} \right)$$

when expressed in molar quantities.

VANHOOK and BRUNO^{18c} and VANHOOK and FRULLA^{18b} have tested this expression with respect to the three independent variables and found only approximate agreement with the stipulated form. At constant temperature, for instance, they assumed that the preexponential factor and the σ factor would remain constant. In that case a plot of $\log J$ against the reciprocal of the square of the log of the degree of supersaturation should be a straight line. This was only approximately the case. DUNNING^{3b} has pointed out that g will depend upon the supersaturation in such a way that $\log J + 3 \log \log c/c_\infty$ should be employed in place of $\log J$ in the linearity test. Another improvement, suggested by the basic theory, is effected by employing activities in place of molar concentrations. In this way satisfactory agreement with the theoretical equation is realized, in so far as supersaturation is involved (Fig. 3/8).

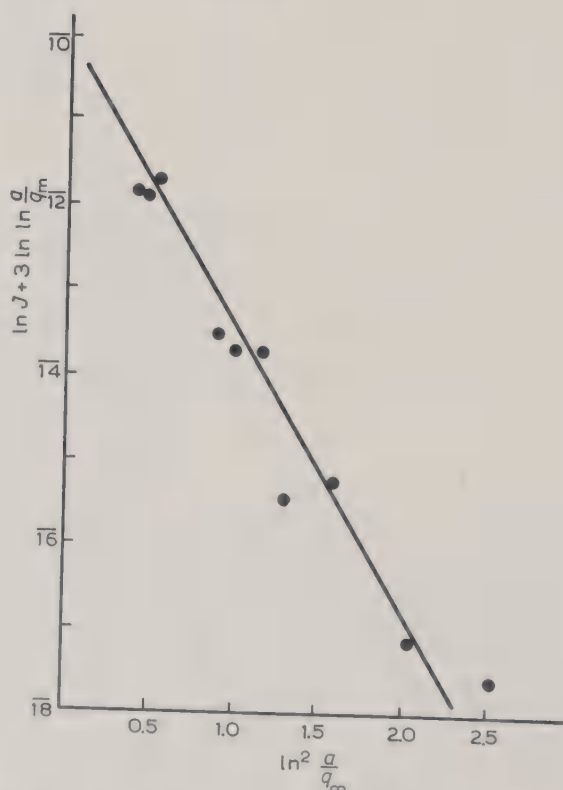


Fig. 3/8. DUNNING and SHIPMAN's test of the nucleation equation^{3b}.

The influence of changing temperature on nucleation rate is qualitatively in agreement with the above expression. However, the quantitative comparison is unsatisfactory even after correcting for the temperature dependence of g , according to DUNNING. The data have been interpreted, therefore, in terms of the overall ARRHENIUS theory of reaction rates^{18b}. Observations of the nucleation rates of syrups from -10° to 40°C may be represented by an activation energy of 4.4 kcal/mole, according to Fig. 3/9.

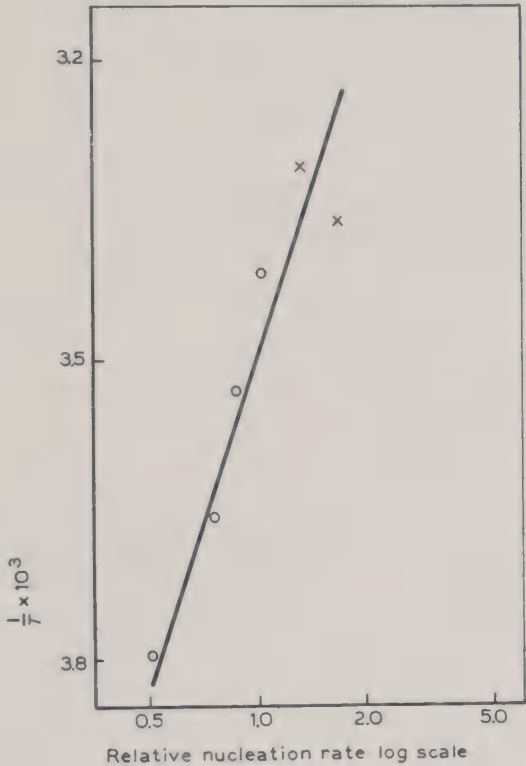


Fig. 3/9. Activation energy of nucleation of sucrose solutions^{18b}. x: bulk samples, o: minimum size droplets.

This value is exactly in the range computed from the temperature coefficients of viscosity and diffusion of these same syrups. This correlation suggests the importance of the transport step in the nucleation process, in contrast to its relative unimportance in the growth process under similar conditions.

In fact, this influence of viscosity is probably the reason for the unsatisfactory compliance in the above concentration and temperature tests. BECKER and DÖRING²⁰ have pointed out that viscosity adds another exponential term of the form $\exp\left(\frac{-E_{\eta}}{kT}\right)$ to the usual kinetic equations. While the original deviations are lessened by such a factor, the improvement is still

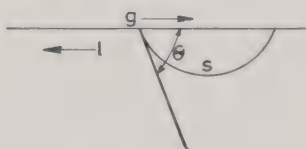
inadequate. It is possible that at least a part of the discrepancy may be due to inadequate viscosity data at these high concentrations²¹.

The σ term in the nucleation equation suggests that the interfacial tension should be a very significant factor in the formation of sucrose crystals. The nucleation rate should increase very rapidly with any reduction in this term. This profound effect in the behavior of ordinary sugar syrups is reported by several workers^{10, 18d, 22, 23, 24, 25, 26}; but was not found by VANHOOK and BRUNO^{18c} when using very carefully prepared syrups free from all extraneous matter. These investigators did observe, however, that the crystal density was prolific when crystallization occurred in the presence of substances which presumably had diminished the interfacial tension factor²⁴.

KING²⁷ reports that surface active agents accelerate the crystallization of sugar solutions, although VANHOOK and FRULLA^{18b} did not find this to be marked when the seed density was very high. Neither is the rate of growth of single crystals speeded by the addition of these materials^{18e}. It is therefore suggested that the benefits of surface active agents are due to their dispersing action rather than directly to an increase in the homogeneous nucleation rate. The general principles of such a heterogeneous reaction have been indicated, but have not yet been applied to the case of sugar syrups.

In the meantime, the lack of agreement between theory and observation suggested a more critical analysis of the σ factor as it occurs in the nucleation rate equation^{12, 18f}. This is a difficult property to ascertain directly. In fact, it is usual to employ the ordinary surface tension in place of the interfacial tension in calculations of this kind. While this is a legitimate value in the case of g-l transformations, it may not fit the case exactly when substituted for other types of change.

The case of a solid appearing within a liquid is equivalent to that solid at the liquid-vapor interface; namely



The DUPRÉ triangle of surface forces for this situation is

$$\sigma_{gl} = \sigma_{sg} + \sigma_{sl} \cos \theta$$

The σ 's are the interfacial tensions at the respective gas, liquid, and solid surfaces, and θ is the angle of wetting. The s-l interfacial tension is identical

with the ordinary surface of the liquid (σ_{gl}) only if the wetting is complete ($\theta = 0$), and the solid itself has no surface tension. The first requirement seems reasonable for a solid in its saturated or oversaturated solution, but the second is questionable. It is, however, reasonable to expect that σ_{sg} is essentially a constant for solids. In that case we would expect a direct correlation between the interfacial tension of a solid in liquid (σ_{sl}) and the surface tension of that liquid (σ_{gl}). Any material lowering the surface tension of a supersaturated syrup would, therefore, be expected to increase its crystal forming propensity since the interfacial tension of the crystal is also lowered.

Before describing the experimental investigation of this proposal it may be of interest to pursue this same line of thought in a qualitative and semi-quantitative explanation of the condition of supersaturation in sugar solutions. The analysis^{18f} was suggested by an equivalent computation suggested by DEDEK²⁸.

In the present form, the GIBBS' adsorption equation

$$T = - \frac{1}{RT} \frac{d\sigma}{d \ln c} = - \frac{c}{RT} \frac{d\sigma}{dc}$$

is used in place of the thermodynamically related GIBBS-THOMSON equation. T is the surface excess, which in the case of a solution may be regarded as a measure of the difference in concentrations of the surface and bulk parts; σ is the tension at the interface or the ordinary surface tension in the model under consideration; c the concentration in the bulk solution; and R and T the usual gas constant and temperature, respectively. In words, the equation states that if the surface tension of a solution increases with the concentration of solute, the relative concentration of this solute in the surface layer is less than in the body of the solution. Pure sugar solutions as well as many aqueous solutions are this kind; and their surfaces may be regarded as undersaturated when the main solution is saturated. Any incipient crystal formed would therefore dissolve in the surface layer. Growth would ensue only when the concentration in this otherwise undersaturated state becomes equivalent to the solubility in the ordinary state. It will be perceived that the mechanism outlined is equivalent to the previous interpretation in which the critical nucleus was employed in place of the solubility. The present description may be applied numerically as follows. The change in surface tension with concentration for sucrose solutions is $d\sigma/dc = 0.03$ when σ is expressed in ergs/cm², and c in g sucrose/100 g water. This value is estimated from the data of SMOLENSKI²⁹, BIGGINS and

VANHOOK^{18d} and others, and is valid out to about 70° brix at ordinary temperatures. Thereafter the values appear to fall from linearity. When this coefficient is inserted in the above equation the result is: $\Gamma = -1.2 \times 10^{-12} c$. At saturation at 30° C, $c = 220$, and Γ calculates as -2.66×10^{-10} ; which means that the surface concentration is less by this amount from the equivalent two dimensional concentration within the bulk of the liquid.

The possibility of forming a supersaturated solution may then be considered as due to the dissolution in this undersaturated layer of the embryo just formed within the bulk solution. This metastable condition will prevail until the concentration is increased to the point where this interface is just saturated. The bulk concentration would then correspond to the supersolubility limit.

To approximate this condition we assume, with DEDEK, that the minimum stable solid nucleus in the bulk solution is a pair of sucrose molecules as found in the unit cell. At a density of 1.58 this calculates as a sphere of radius 5.5 Å. The cross section will be $94 \times 10^{-16} \text{ cm}^2$, and a mole of sucrose will be $N/2$ of these pairs covering $282 \times 10^7 \text{ cm}^2$. The reciprocal is $3.5 \times 10^{-10} \text{ moles/cm}^2$. The surface layer concentration is 2.7×10^{-10} less than this concentration, or the degree of supersaturation in two dimensions is

$$\frac{(3.5 - 2.7) 10^{-10}}{3.5 \times 10^{-10}} = 23\%$$

Since the surface deficit is proportional to the bulk concentration, we may say that the surface layer will attain the normal solubility in two dimensions that is equivalent to the bulk solubility when the bulk concentration is about four times its normal value.

This is considerably larger than the 1.6 observed experimentally but is entirely reasonable when we consider the approximate nature of the calculation. It is also likely that the surface tension-concentration coefficient used is too high. This possibility is within the uncertainty mentioned in the literature. It would only be necessary to halve the value employed (0.03 to 0.015) to arrive at reasonable figures for the critical supersaturation. Twenty molecules per critical nucleus, instead of two, is the result of the calculation employing the given surface tension coefficient and a metastable limit of 1.6.

Return now to the consideration of the surface tension behavior of sugar solutions. Pure sucrose is surface inactive in the sense that it increases the surface tension of water slightly as the concentration is increased²⁹. On the other hand, natural sugar juices, and even ordinary refined sugars, are

surface active in that such solutions may have surface tensions considerably less than that of water. This is illustrated in the Fig. 3/10. Curves *a* and *b*

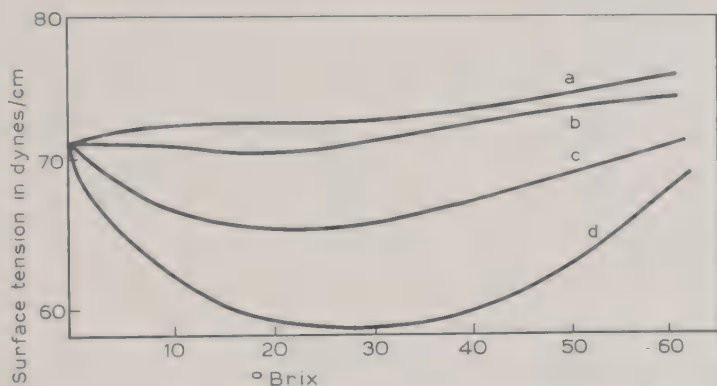


Fig. 3/10. Surface tension-concentration relationship of beet sugars⁸⁴. *a* and *b*: refined grades, *c* and *d*: direct consumption grades.

are refined sugars, while *c* and *d* are direct consumption grades. Natural juices and molasses conform to the latter types with the minima varying in location according to the quantity of colloidal material present. The effects of particular surface active materials are represented by the typical results of Fig. 3/11. The full curve of Fig. 3/12 illustrates the minimum

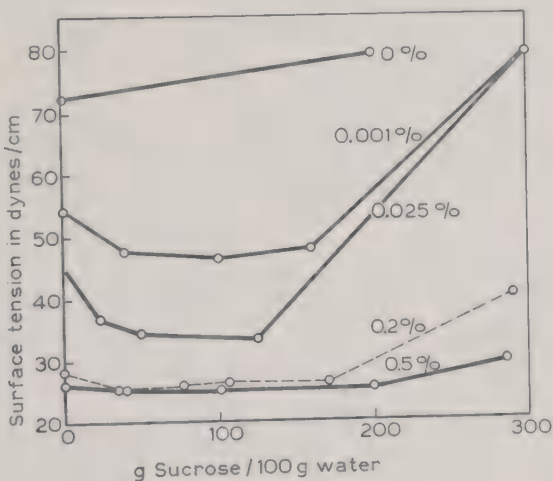


Fig. 3/11. Effect of sucrose on the surface tension of solutions of aerosol O.T. Static (ring) values, corrected. Surface active agent concentration based on aerosol water^{18d}.

in the surface tension-dilution curve of a cane molasses as well as the fact that added sucrose increases the surface tension. In all cases examined to date, whether natural or synthetic syrups, it has been observed that the

surface tension is not greatly different from that of pure sugar solutions when the total solids has been increased to the supersaturation level.

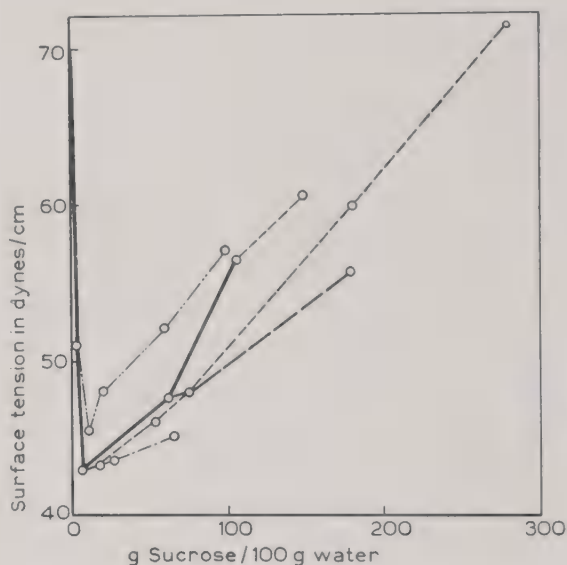


Fig. 3/12. Surface tension of a Cuban cane molasses. Static (ring) values, corrected. — = diluted stock, ---- = sucrose added. Pendant drop values are about the same at the minimum, but decrease to 13 dynes/cm less for the stock solution (106 g sucrose/100 g water)^{18d}.

This effect refers to the ordinary static, or equilibrium, value of the surface tension, and is determined on aged surfaces by methods which do not disturb them. The dynamic, or immediate, surface tension may be higher than these equilibrium values, and is dependent on the age of the solution. This is illustrated in Fig. 3/13 for a particular beet molasses. The momentary surface tension augments the already high static values of supersaturated

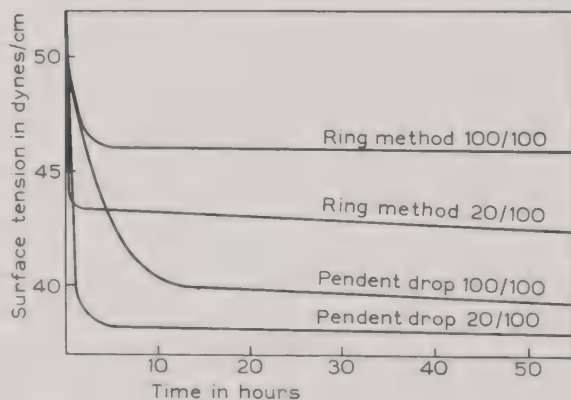


Fig. 3/13. Surface tension-time relationship of diluted beet molasses. Original stock: 273 g of sucrose and 183 g of non-sucrose per 100 g of water. Concentrations in g of sucrose/100 g of water^{18d}.

sugar solutions, so that in reality the dynamic surface tension has not been changed significantly even upon addition of highly active surfactants. This condition is emphasized with regard to the dynamic values, and this, rather than the static value, would seem to be more significant in problems of crystal generation and growth. Judicious considerations of surface tension factors are discussed by CASSEL and LANDT¹⁰, and by CAPELLE²³. The relative indifference of the rate of crystal generation in the presence of surface active impurities thus appears reasonable in spite of the strong influence of the σ^3 term in the rate equation.

Several provocative computations can be performed with the above equations and the sparse data which are available for supersaturated sugar syrups^{3, 18}. The slope of the appropriate plot of nucleation rate against supersaturation yields a value for the interfacial tension, σ ; while the intercept defines the transition probability, g . DUNNING and SHIPMAN^{3b} found these to be 4.6 to 4.8 ergs/cm² and approximately 10^{-5} , respectively; while VANHOOK and FRULLA¹⁸ reported 6 ergs/cm² for the first parameter and approximately the same 10^{-4} to 10^{-5} for the latter.

The energy estimate is within the rather wide limits allowed for this property and is compatible with the usual values of 10–100 ergs/cm² ordinarily allotted to s-g surface tensions. If the computed values are inserted in the GIBBS-THOMSON equation, one computes that the radius of the critical nucleus is about 19 Å. This is equivalent to a sphere containing about 80 sucrose molecules and is comparable to the estimates in other systems³⁰. This critical size is much smaller than the 14×10^3 Å inferred for sucrose by SCHWEIZER³¹, and larger than that assumed in the previous calculation (see p. 128). Recent considerations of the kinetics of ionic precipitations also indicate much smaller values of the critical nucleus than those realized by calculations of the above kind. The entire problem needs renewed attention and analysis³².

The pre-exponential value is low, and signifies that the expectation for the continued growth of the critical nucleus is small compared to the frequency with which it disappears by dissolution. The transition state theory of reaction velocity as applied to the case under consideration amounts to

$$J = \frac{kT}{h} \cdot \exp\left(\frac{\Delta S^*}{R}\right) \cdot \exp\left(\frac{-\Delta H^*}{RT}\right)$$

where the first factor is a universal frequency term, and the second an orientation factor. The observed value of the combination requires an extremely high entropy change for the process. This is not unreasonable

when the symmetry of the sucrose crystal is considered together with the fact that several water molecules associated with sucrose in solution must be excluded in crystal formation. This situation is not unusual³³, and serves to emphasize that even quasi-equilibrium conditions may not be realized during the birth and growth of crystals. The pressing need for dynamical treatments of the problem is inferred in recent discussions^{4, 32, 34, 35}.

4. Experimental Methods and Results

(a) *Nucleation Experiments*

The theory of nucleation is more highly developed than theories of growth, at least in their modern forms² and until recently³⁶. On the other hand and for condensed systems, the experiments on crystal growth have exceeded those on generation. This situation is especially true with regard to sucrose solutions. An abundance of papers on the growth of sugar crystals is available whereas relatively few on nucleation are recorded.

The word *sugar* itself stems from the Sanskrit *sarkara*, meaning little pieces, gravel, or granulation. The early processors and refiners of sugar were well acquainted with the crystallizing behavior as expressed by the term *graining*. This was first presented in exact quantitative meaning and appreciation by CLAASSEN, according to WEBRE¹⁷. The contribution of THIEME³⁷ and KUCHARENKO³⁸ soon followed and supplied the sugar technologist with complete and detailed data and discussions of the science and practice of sugar boiling. Both these manuals are still appropriate and adequate. These expositions of the crystallizing behavior of sugar syrups applied the supersolubility as had been developed by OSTWALD, BERKELEY, TAMMANN, FOUQUET, and others.

KUCHARENKO's ideas on the constitution of strong sugar solutions are most intriguing. He recognized the difficulty and almost impossibility, of avoiding accidental inoculation of supersaturated sugar solutions; thus accounting for the observation that such supersaturated syrups almost inevitably deposit crystals. Yet, under virtually aseptic conditions, this adjustment may be postponed even indefinitely^{18a, 28}. KUCHARENKO accounted for this in terms of the *crystallones* and *colloidones* which he regarded for the structural units of solution. The former were defined as 'minute particles not to be discerned by the strongest microscope but conserving nevertheless all the properties of a large crystal, and colloidones, particles losing the essential properties of a crystal'. In modern chemical terms these designations express the associated condition of sucrose in solution which progressively increases as the concentration becomes greater. The crystal-

lone is an aggregate considerably larger than the colloidone and may even grow to become an embryo or germ and eventually true nucleus and crystal. The physical state visualized is equivalent to the current disorder-order concept and to the equilibrium $nA = A_n$ which has already been used to represent the consolidation of molecules in the critical nucleus.

KUCHARENKO postulated that crystals or even crystallones could separate into smaller fragments which in turn would grow to larger sizes by accretion of colloidones and molecules. This is quite a vivid description of the mechanism of 'false grain' formation.

FOUQUET's³⁹ early paper in the *Nucleation of Pure Sugar Syrups* warrants consideration. Some of his observations are given in Table 2. FOUQUET's solutions were very carefully prepared and cooled slowly with gentle

TABLE 2
NUCLEATION OF PURE SUGAR SYRUPS³⁹

Sugar/100 g Solution	Water	Temperature, °C		Sugar/100 g water		Degree of supersat.
		Sat.	Crystallization	Sat. soln.	Excess	
78.7	369.4	81.5	31	221.3	148.1	1.66
79.8	395.0	86.5	44.2	247	148	1.60
80.8	420.8	91	54.4	271.6	149.2	1.55
82.4	468.1	97.5	69.5	318.7	149.4	1.47
83.0	488.2	100	75.0	339.8	148.3	1.44
84.8	557.9	—	88.5	406.9	150.3	—
85.1	571.1	—	92.0	428.8	142.3	—

agitation. The temperature at which crystals first appeared were noted. FOUQUET pointed out that his observations were in complete accord with those of MIERS who worked principally with salt solutions. VANHOOK has computed FOUQUET's results in terms of degrees of supersaturation. The values in the last column are approximately in the range previously designated for homogeneous nucleation. He has also computed the activation energy from this data and obtained a value of 2.4 kcal/mole. This is somewhat less than the 4.4 already mentioned but does serve to emphasize the difference with the activation energy of growth.

The next nucleation studies specifically on sugar solutions are those from the Delft laboratory⁴⁰. These workers did not note the temperatures at which crystals developed in a cooling syrup as did FOUQUET, but rather the time at which crystals appeared at constant temperatures and constant supersaturation. VANHOOK has computed that the data of these two papers, which cover from 40°–90° C, may be represented by an equation of the form $(O-a)t$ equals constant, with a equals 1.37. O is the supersaturation

and t , the time. a is then the supersolubility or metastable limit. The activation energy of the process was also estimated to be about 5 kcal/mole.

Later work from the laboratories of DUNNING and VANHOOK have already been mentioned in the theoretical section. On the experimental side they emphasize the absolute necessity of 'curing' the syrups in order to realize true homogeneous nucleation. The curing consists of heating the syrup for at least 20–30 minutes at temperatures at least 20–30° C in excess of saturation. This treatment is required in order to (1) completely dissolve the solute – the last traces of sugar are reknowned for being reluctant to dissolve; (2) to destroy all transitory order in the saturation region; (3) to inactivate accidental foreign particles. These requirements or at least the first two may also be fulfilled by vacuum evaporation³¹ of dilute solutions, but the operation is not performed as conveniently as treatment by heat. It is also advisable to avoid foreign 'dust' particles, since these are not always completely deactivated by the usual treatment. In that case a preliminary 'shower'^{8, 39, 40} is observed which may not interfere with the nucleation measurements at high concentration, but will destroy the ability of only slightly supersaturated solutions to remain virtually permanent. These showers first 'light' and then 'heavy' are prominently revealed in cooling experiments of the FOUQUET type. The first one occurs upon passing into the metastable range, when slow growth ensues upon any active foreign particles that may be present; the second dense shower signals the onset of rapid growth upon entering the intermediate or labile zones according to whether foreign nuclei are present or absent. At this time the autocatalytic nature of nucleation is beautifully displayed.

The aforementioned workers used two different, albeit equivalent, methods of expressing the nucleation rate of sucrose syrups. DUNNING and SHIPMAN counted the total number of crystal centers in a syrup at different times and considered the slope of the linear population curve as the nucleation rate.

VANHOOK and co-workers, on the other hand, noted the time of appearance of the first crystal and regarded this induction period as inversely proportioned to the nucleation rate. However, it was recognized that a definite period of time was required for the invisible critical nucleus to grow to visible size. The correction was suggested by the methods employed by VAN GINNEKEN and WATERMAN⁴⁰. A clean, single crystal was touched to syrup of different concentrations and the time noted for a microcrystal to appear at this point. These incubation periods were essentially the same as those reported by the Dutch workers.

The results illustrated in Table 2 were obtained on stirred solution. FOUQUET remarked that lower and inconsistent values were obtained when

the syrups were not agitated. The Delft workers also employed slow rotation of their sample in order to assure reproducible results. FOUQUET also mentions the occurrence of the preliminary shower as described above. VAN-HOOK concurs in these observations but in addition has observed that different rates of rotation have no appreciable effect on the nucleation time when the solutions were entirely free from suspended material and well cured. Neither does glass propeller stirring, under oil, up to 300 r.p.m. and below $S = 1.4$. Above this concentration, however, the nucleation times were greatly reduced the higher the concentration and faster the stirring. For instance, at S equals 1.4, stirring at 300 r.p.m. for two days did not especially encourage crystallization. At 100 r.p.m. a 1.5 supersaturated syrup crystallized in $4\frac{1}{2}$ hours, whereas without stirring or with gentle rotation it is normally stable for weeks. At S equals 2.0, where unstirred solutions take about a day to develop a visible crystal, a cloud shows up within a few hours at 100 r.p.m. and in about an hour at 300 r.p.m. Any accidental contact of the stirrer with the sides of the container or with added glass beads induces crystallization very promptly even at low supersaturations.

These irregular results with stirring suggest the influence of viscosity; which factor was investigated by means of the temperature coefficient of reaction. As already mentioned, the activation energy turns out to be about 5 kcal/mole. This is exactly the magnitude allowed for transport processes and indicates the operation of this factor in the nucleation process (see later sections on mechanism of growth.) POWERS⁴¹ describes the appearance and growth of crystals in stirred syrups as well as those which have been gelled by the addition of gum arabic. Further experimentations along these lines should prove most revealing in the interpretation of the mechanism of nucleation as they have already regarding growth.

The sensitivity of sugar syrups to mechanical influences was demonstrated in a vivid way by BERKELEY in 1912⁴². A solution which formed crystals at 6.5° C below its saturation temperature was made to crystallize at only 3 degrees supercooling when subjected to intense mechanical stress. The stress was produced by the motion of a brass piston rod as well as by the impact of a small trip hammer upon an anvil. This behavior was confirmed in many other melts and solutions by YOUNG and VAN SICKLEN⁴³. WOOD and LOOMIS⁴⁴ in their exploratory investigations of the properties of ultrasonic waves also noted that this radiation was able to induce the formation of crystals in a supersaturated $\text{Na}_2\text{S}_2\text{O}_3$ solution. Numerous researches have since amply confirmed the general accelerating effect of this form of energy in the production of crystals from appropriate mother

liquors⁴⁵. It is not always clear that distinction is made between the two consecutive and simultaneous steps of the crystallization process, but it is most certain that irradiation does increase the net rate of adjustment of many supersaturated solutions and supercooled melts⁴⁶.

Sugar solutions confirm the general pattern of instability under the influence of intense irradiation. The first recorded tests with sound, to the writer's knowledge, are those of ASTOLFI⁴⁷, some German developments during the last war⁴⁸, and of GALKOWSKI⁴⁹ in the laboratory of the Holy Cross College. The positive effects of increased crystal growth have since been confirmed in several laboratories and the recent developments have been reviewed on different occasions⁵⁰. In brief:

(1) The mechanism of sound activity is heterogeneous, and not homogeneous.

(2) Treatment with sonic waves accelerates the adjustment of supersaturated sucrose solutions, both pure and impure. This treatment has no special effect on the rate of growth of single sugar crystals, so that the observed overall increase is due almost entirely to enhanced nucleation by false grain formation.

(3) The effects of sonic graining become more pronounced with increasing supersaturation and time of irradiation. A threshold power level of about 2 sonic watts/cm is necessary to obtain any significant results; excess energy above this level is relatively ineffective. The optimum frequency is in the neighborhood of 10 Kcs. No unusual effects have been observed over the temperature range 30°–70° C.

(4) It has been observed also that many substances which are reluctant to crystallize under ordinary conditions frequently deposit crystals soon after irradiation, *e.g.* L-arabinose, sorbitol, DL-glyceraldehyde, D-gluconic acid, brucine, and many others^{18b}.

This ability of sound waves to stimulate crystallization may prove to be a benefit to the preparative organic chemist especially in the field of sugar derivatives.

The practical value of the process is attested by the existence of several patents^{47, 51, 52}.

Benefits are not merely the overall acceleration of growth, but the fact that footings can be established almost immediately. This improved grain uniformity should lead to improved boiling and also better and quicker separation in the centrifuge.

(b) *Impurities*

The rates of nucleation of sugar syrups are impeded by the addition of

non-sucrose solutes. This is reflected in the increase of the OSTWALD supersolubility limit when passing from high to low purity stocks. GILLET⁵³ states that 'in Crockett's experience the safe upper limit of the metastable zone for white massecuites is regarded as fringing on a supersaturation limit of about 1.4–1.5. In low grade work this limit of the metastable zone

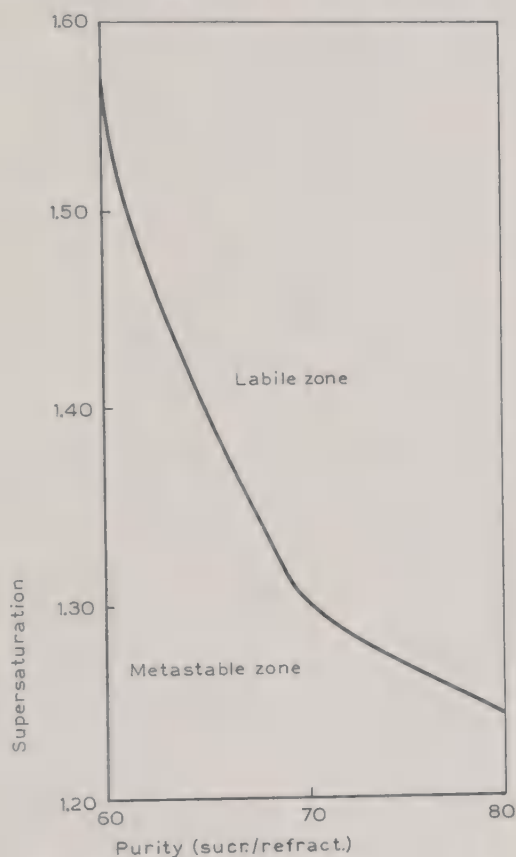


Fig. 3/14. Supersolubility-purity relationships⁵⁵.

may be 50% higher'. CAMERON⁵⁴ places the limit between 1.40–1.45 at 140–145° F and 60–70 purity; the intermediate zone between 1.40–1.45 and 1.60; and the labile above 1.55–1.60. DAVIES and YEARWOOD report that the approximate metastable limit of about 1.3 for pure syrups is increased

TABLE 3
EFFECT OF TEMPERATURE ON THE UPPER LIMIT
OF THE METASTABLE ZONE, 60 PURITY⁵⁵

Temp. °F	Supersaturation
141	1.55
158	1.50
172	below 1.50

with decreasing purity, but that temperature has little influence on this effect. Their results are illustrated in Fig. 3/14 and Table 3.

WEBRE mentions comparable increases in his numerous writings on sugar boiling¹⁷. Other sugar technologists find similar results for a variety of sugar house liquors^{37, 54}. NAVEAU²², however, cites HONIG's experience that 'le degré d'impureté du sirop dense stimule la formation du grain'. VANHOOK confesses a dearth of experience with natural syrups but casual experiments indicate to him that most ordinary impurities appear to postpone the onset of crystallization. Separate experiments with surface active agents have already been described. In summary, they reveal that the small amounts of surfactants needed to reach the critical micelle point have relatively little effect on altering the metastable limit of sucrose syrups. However, at this point these agents appear to enhance the crystal seed density tremendously (see p. 126). Further quantitative studies in this direction are needed.

It is also interesting to observe in this connection, and possibly not entirely irrelevant, that these surface active agents have a pronounced effect upon crystal crops obtained in their presence. Even with white syrups the crystals obtained are considerably improved in appearance and quality. The tendency to agglomerate and aggregate is reduced.

This is illustrated in Fig. 3/15. These are schematic growth curves of

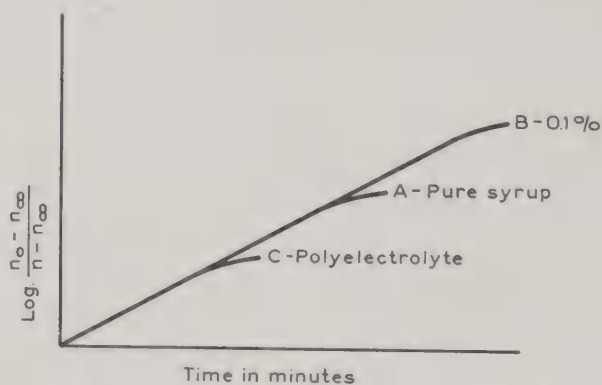


Fig. 3/15. Crystallization of seeded syrups by refractometer^{18f}. B: added surface-active agent.

seeded syrups, obtained by refractometric analysis. The usual curve *A* for white syrup is linear in terms of monomolecular growth over a considerable period. When $\frac{3}{4}$ of the crystallizable sugar has deposited, the growth rate diminishes because the crystals grow together and diminish the surface available for continued deposition. Even a small amount of surface active agent (*B*) postpones this action considerably. It has been the impression

from work in the laboratory of the Holy Cross College that nonionic agents are more beneficial than ionic ones in this respect. The aggregation may be aggravated (*C*) by the addition of coagulating agents, in which case the deviation from linearity sets in early in the adjustment.

(c) *Foreign Particles*

Foreign particles generally antagonize the persistence of the metastable state and sugar syrups are no exception to this rule. Turbidity, and even discreet suspended particles, are often visible in strong solutions of many refined sugars. Such solutions are apt to crystallize more readily than comparable solutions in which suspended material is not visible or the same syrup after filtration or centrifugation. The same improvement may also be accomplished in some cases by 'curing'. This beneficiation may be only partial according to the extent of the treatment. VANHOOK has encountered instances of syrups which contained considerable amounts of suspended material (lint) whose nucleating behaviors were improved as much by prolonged curing as by filtration. However, it is advisable to utilize absolutely clean solutions for nucleation experiments in order to avoid the uncertain influence of foreign suspended particles.

Many early workers have reported that melts or solutions once crystallized may be reluctant to enter the supercooled or supersaturated state again. They describe this remarkable behavior in terms of the 'memory' of the system. It appears reasonable that the effect may be ascribed to the order-disorder phenomena which occur in the neighborhood of transition points⁵⁸. On the other hand, foreign particles may also be a contributing factor, according to the following singular experiences.

The nucleating behavior of a syrup made from a beet molasses was being studied by observing the time required for crystals to appear. The times observed in the first trials were frequently much longer than those noted upon repetition. For instance; when the original stock was dissolved and cured at 90 purity and 100% supersaturation, crystals appeared after 3 to 5 days. After redissolving and reheating, only about a day was required. When the sample was centrifuged after only a part of the crystallization had occurred, and the experiment repeated, the crystallization times resumed the initial period of several days. Presumably an impurity was adsorbed on the first crystals and they were not reversibly dissolved in the dissolution process. It therefore remained effective to stimulate the subsequent crystallizations. After removal with the crystallized fraction, the solution regained its original crystallizing tendency.

This is only one particular case illustrating the effect of foreign particles. SPENGLER has noted that CaCO_3 particles are unfavorable for grain formation, while BLAZEK⁵⁹ reports the contrary. NAVEAU²², CASSEL and LANDT¹⁰, and CASSEL and TODT⁶⁰ call attention to the fact that foreign particles may induce false grain. The confectioner uses gums, colloids, and a wide variety of other additives to induce prolific fine grain for his fondants and creams, and yet these same or other agents often prevent the further recrystallization that leads to coarse grain. These are probably behaviors which involve foreign bodies as well as the influence of interfacial tension. This latter factor has already been intimated^{3a}.

The writer knows of no recent complete discussion and analysis of this problem, but would presume to mention several observations that may be pertinent. The fact that crystals are attached to the string at the left, truncated (1 $\bar{1}$ 0) end, in the ordinary process of making rock candy, is probably significant. WILLEMS⁶¹ and NEUHAUS⁶² discuss oriented overgrowths of and on sucrose. Adsorption⁶³ and epitaxy³⁴ may also play dominant roles in this connection. CAPELLE²³ reports that sugar crystals deposit on only one of two electrodes inserted in a growing syrup, and that a potential of 3–5 mV is established. It is also observed that sugar crystals often ‘stick’ to the walls of glass or metallic containers. This condition may be alleviated by the addition of small amounts of surface active agents or by ‘siliconing’ the surface. The attachment is also considerably less on non-wettable surfaces such as polyethylene, wax, etc.

(d) *False Grain*

False grain or smear is no illusion to the sugar boiler. It is encountered in the upper regions of the metastable zone and conditions of juice nature, boiling procedure and pan design are known to affect its occurrence. Generally, false grain may be avoided by good boiling practice.

The intermediate zone of concentration, in which false grain forms, is defined as the concentration range within which added crystals not only grow, but also multiply. Without added crystals no unusual activity occurs in this territory. There is no need to add crystals for growth if the syrup is in the labile zone, for here the growing base is provided by spontaneous generation. The growing crystal will multiply in this case just as in the seeded intermediate zone. It is obvious then that false grain is not confined to the intermediate region alone, but is common to the labile area also. It therefore follows that false grain is a corollary of growth, and its explanation is to be sought in the mechanism of this process. This is essentially the

interpretation of VAN GINNEKEN⁴⁰ to which VANHOOK has subscribed^{18g}.

If this is the case, the intermediate zone as delineated in the supersolubility diagram loses some distinction on account of this secondary nature. DAVIES⁵⁵ concludes ‘that the intermediate zone as defined by WEBRE is so narrow in extent as to be of little practical importance’. He observed that the metastable range at high purities was considerably less than at low purities, and expected a similar spread for the intermediate zones. Yet at 60 purity this zone extended at most only 0.07 degrees. WEBRE himself¹⁷ implies the same by recognizing ‘that the inevitable time element also has an important bearing upon crystallization, and that if this time is short enough it is actually possible to enter the labile zone without inducing the formation of nuclei’. GILLET⁵³ makes no particular distinctions in this region of the super-solubility diagram.

POWERS⁴¹ has already presented a vivid and detailed picture of the process of crystal growth. The regular and layer-like addition of sucrose molecules which he now records for the first time is a necessary prerequisite for the development of a good, clean, single crystal. This specification is not always met readily with sucrose, and even with crystals at large³⁴. Growth is more frequently irregular and sporadic, unless very carefully controlled and regulated^{64, 65}. The aberrations become magnified as the growth rate increases. VANHOOK has referred to this situation as resulting from dendritic growth^{18g}, although true dendritic habits are not necessarily observed⁴¹. Highly oversaturated syrups ($S > 1.2-1.3$) appear to form new centers of growth on or near the surfaces of growth. These nodules then appear to be swept from the surface, especially with agitation, and give

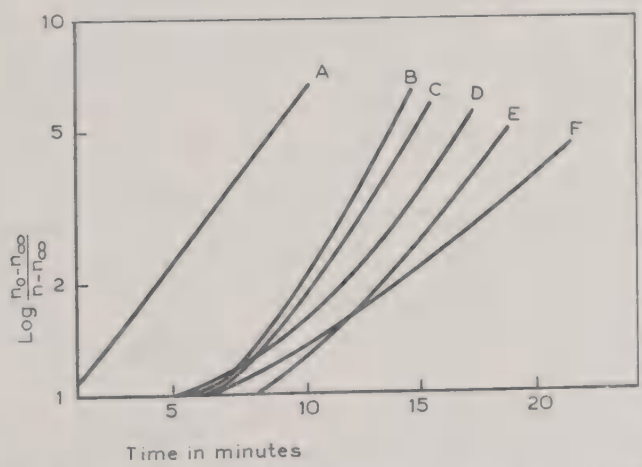


Fig. 3/16. Effect of stirring speed on crystallization rate of sucrose. $S_0 = 1.16$, 30°C , $1/20$ of 40–60 mesh seeds. A: $1/15$ of XXXX seed, directly on refractometer prism. B: 400 and 500 r.p.m., C: 250 r.p.m., D: 150 r.p.m., E: piston stirrer, F: 85 r.p.m.

rise to brand new crystallites, or false grain. This action appears to be accentuated at and near corners and edges. False grain then appears to result from the erosion fragments which inevitably attend rapid growth^{18g, 41, 66}.

In this case one would expect false grain formation to depend upon agitation; and the influence of circulation is well recognized by the sugar boiler⁶⁷. Fig. 3/16 illustrates this effect on an experimental scale. The curves represent growth in seeded solutions, and both the slope and intercept are measures of the total growing area. This surface is related directly to the number of growing crystals, or false grain. The progressive decrease of slope and corresponding increase in incubation period from curves *B* to *F* are indicative of the dependence of false grain formation on stirring. Similar results have been reported for other systems^{43, 68}.

It is also observed that sugar crystals can be disintegrated by agitation in saturated syrups even at slow stirring rates⁴¹. The alteration depends upon the intensity of stirring, the supersaturation, and the crystal population. Small glass beads or other hard objects may be substituted in the last instance with the same results. It seems clear then that attrition of growing crystallites contributes significantly to the formation of false grain. On the other hand, it must not be overlooked that some circulation is necessary to avoid aggregation and agglomeration. In practice forced circulation appears to offer pronounced benefits¹⁷.

McGINNIS⁶⁷ lists the conditions contributing to false grain formation as follows:

(1) Too coarse grain, *i.e.*, too few nuclei formed in the graining period. Under this condition a too small area of crystal surface is available for crystallization, the crystals are too far apart, and the rate at which the mother liquor is desugared is too slow for the rate of concentration by evaporation. In this case, the situation may be remedied by slow boiling at lower supersaturation at the expense of time. Too many crystals may also lead to false grain as discussed above. THIEME³⁷ discusses this situation from the factory angle.

(2) Too rapid boiling, resulting in too high supersaturation.

(3) Insufficient circulation.

(4) Turbid feed syrup. When the standard liquor filtration is inefficient, allowing small particles to pass into the pan in the feed syrup, it has been shown that the particles may serve as effective points for new nucleus formation.

(5) Grain in feed syrup. This condition is normally encountered only in remelt boiling. Small crystals inevitably pass through the centrifugal screen. These should be removed by diluting the machine syrup to undersaturation before it is used as pan feed.

(6) Air leaks. Air leaks into the pan may shock the syrup, giving a continual crop of new nuclei.

From the factory operator's point of view, false grain is objectional because it represents a loss in sugar recovery and because it impedes purging in the centrifuge.

The occurrence of false grain at high supersaturations follows directly from the theory of nucleation already outlined and from that of growth to be described in the next section. Nucleation is critically dependent on concentration and becomes almost explosive at a degree of supersaturation of 1.5 to 1.6 when the process is homogeneous. In the presence of foreign bodies, of which already existing sucrose crystallites are only one example, the pattern is the same but at a much lower level. Growth, however, is less critically dependent on the concentration. This difference is illustrated schematically in Fig. 3/17. The net adjustment in any seeded solution will be the combined result of these two processes, and will exhibit a rapid

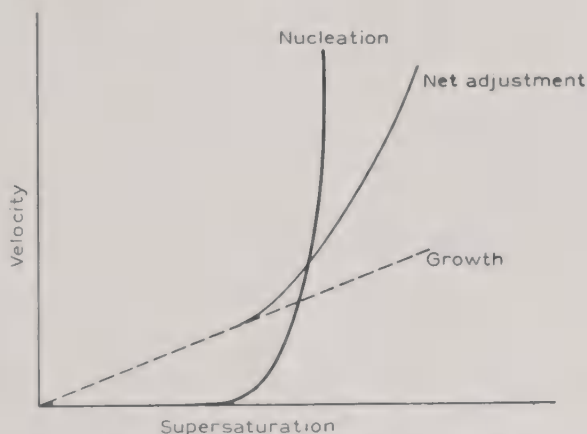


Fig. 3/17. Adjustment of unseeded syrups (schematic).

increase which is tantamount to false grain formation⁸⁵. TAMMANN described this effect in general by pointing out that the maximum in the K.Z. curve is usually much more abrupt than the analogous change in the K.G. curve.

In this respect it must be noted that both the nucleation and growth curves of TAMMANN exhibit maxima which may be explained by the influence of viscosity and heat of crystallization. It has already been noted that these factors may account in part for the form of the nucleation curves of sugar syrups at high concentrations, and it is not impossible to continue the curve of Fig. 3/7 so as to exhibit a sharp maximum. NICHIK⁸³ reports such a strong maximum in nuclei number in sugar solutions of increasing

strength at 70° C. WEBRE¹⁷ suggests the reality of the maximum in the following words: 'It may sound very strange, but actual operation has demonstrated that the formation of new grain will be much more rapid and uniform at a not too high concentration. Actually, if the density is excessive the grain formation may stop altogether, to begin again when the mass is diluted, thus yielding two crops of crystals'. STARE⁶⁹, PALMER⁷⁰, and others have also investigated amorphous sucrose, which state may correspond to the extremes of the TAMMANN diagrams.

VANHOOK, however, regards the pronounced decrease in the nucleation rate at high concentrations the result of the inevitable degradation which attends the production of sugar solutions of this strength^{18a, 71}. Further experimentation at low temperatures may serve to illuminate this intriguing situation.

(e) *Graining Practices*

There are three different techniques for establishing grain. These are the 'waiting', 'shocking', and 'seeding' methods which correspond essentially to operation in the labile, intermediate, and metastable zones, respectively. The grain establishment and selection periods of the strike are critical periods in the boiling schedule which comprise a major part of the art of sugar boiling. The technology of operation in this process is considered in detail in the later chapters as well as in standard treatises on the subject^{17, 28, 37, 53, 66, 67, 72-6, 82}. Suffice it to refer here to only two recent developments pertaining especially to graining.

Full seeding has been used in sugar boiling for a long time, but as ordinarily practiced has certain disadvantages. These are: availability of seeding stock, difficulties and cost of preparation, amounts required, etc.⁵³. These objections may be overcome by employing extremely fine crystals, and this is essentially the main feature of GILLET's system. Powders even finer than fondants are prepared by prolonged ball milling in an inert medium. Isopropyl alcohol and mineral oil have been found to be suitable. The particles produced in this way are in the 5 μ -range; which is considerably smaller than the 40 μ -range of ordinary powders or the usual 20 μ -range of fondants. An advantage of these small sizes is obvious upon consideration of the fact that the number of particles per unit weight varies inversely as the cube of the size. In practice it is found that amounts of seed may be reduced to 10% of previous requirements, and a pound or less of stock may suffice for as much as 2000 cu.ft. of massecuite. Details of this improvement are given in the reference cited above as well as in more recent reports^{77, 78, 79}.

In 1938 WEBRE¹⁷ proposed an improvement of the two-boiling system

which involved making grain on 60 purity molasses rather than on the more pure meladura. The revised procedure increased the efficiency of the boiling step considerably. It was subsequently noted (*ibid.* 1946) that ‘the molasses granulation produced well shaped quadratic crystals free of conglomerates, which purge very well, and possess excellent refining qualities’. Figs. 3/18a

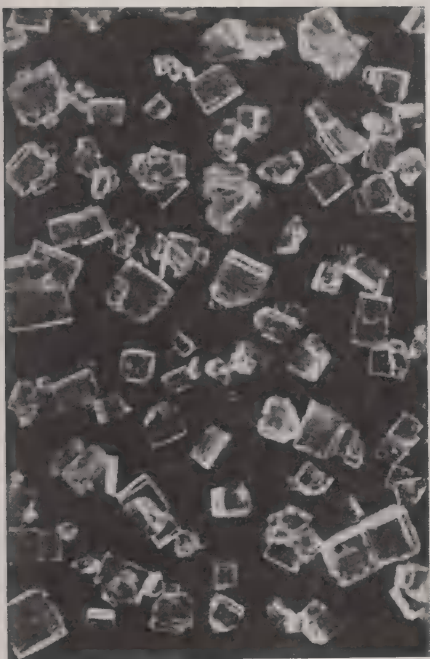


Fig. 3/18a. Commercial bulk sugar.
Seed from A strike at 80 purity.

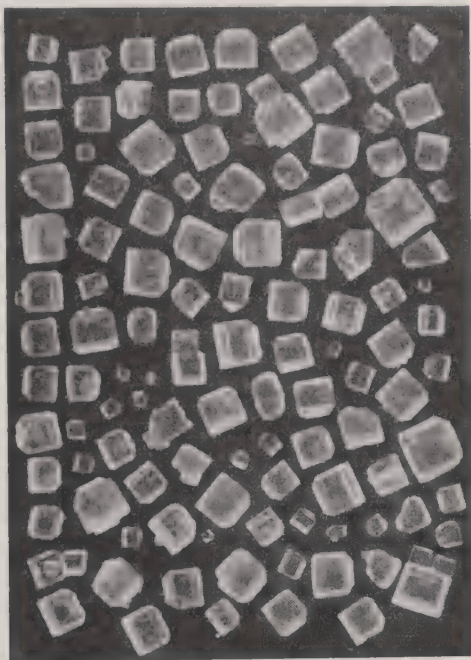


Fig. 3/18b. Commercial bulk sugar.
Seed from C strike at 60 purity.

and 3/18b are typical examples¹⁷. The improvement is presumably applicable at all factory levels^{17, 80, 81}.

The observation is not at variance with the foregoing discussion of nucleation and known facts about conglomeration. It has been pointed out that surface activity appears to reduce aggregation. This correlates well with the recognized principle that this action is more pronounced at high purities. It is also well known that conglomerates are very persistent and difficult to dissipate once formed. The benefits of the method thus appear reasonable in the light of this explanation.

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CHAPTER 4

KINETICS OF CRYSTALLIZATION GROWTH OF CRYSTALS

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1. Introduction

Pan boiling consists essentially of the removal of water by evaporation and the depositing of sugar attending the increasing concentration. This is a set of consecutive processes in which the overall rate of reaction is controlled primarily by the slower step. In sugar work, at least at high purities, the slower step is usually the rate at which solid sucrose can be accommodated on the established footings, so that the rate of growth becomes the dominating factor in the time required for the strike. This situation may no longer prevail at lower purities or other temperatures. Heat transfer coefficients may then be considerably less, with a resultant decrease in the evaporation rate to the point where it may become significant and even prevailing in the total rate of boiling. In any event, this simple kinetic consideration emphasizes the importance of the rate of crystallization for understanding the boiling operation.

The conditions affecting the rate of reaction in concentrated systems are principally temperature and concentration. The first of these is accounted for adequately by the usual ARRHENIUS equation. The second is the net effect of condensation and evaporation when regarded dynamically; or $f(C) - f(C_o)$. $f(C)$ is some function of the concentration in the mother liquor, while $f(C_o)$ is characteristic of the growing unit itself. Since the net growth is observed to be zero when the medium is just saturated, $f(C_o)$ is to be identified with the solubility in the case of solutions. The rate of growth is some function of the supersaturation; $f(C - C_s)$. The simplest explicit form of this function is the linear equation: velocity = $k(C - C_s)$. This equation appears to describe the sucrose — water system adequately. If the degree of supersaturation is defined as $S = \frac{C}{C_s}$, and the velocity is

recognized as the time decrease of concentration, $-\frac{dc}{dt}$, this equation may be written $-\frac{ds}{dt} = k(s - 1)$; where the crystallization potential is the excess concentration or oversaturation.

The above definition of the degree of supersaturation is the one introduced by CLAASSEN, and, as before, is defined as

$$S = \frac{\text{sugar/water ratio in syrup}}{\text{sugar/water ratio in saturated syrup at the same temperature}}$$

The supersaturation has also been utilized in terms of percentage composition, in which case the coefficient of supersaturation is defined as

$$S' = \frac{\text{sugar}/(\text{sugar} + \text{water})}{\text{sugar}/(\text{sugar} + \text{water}) \text{ saturated at same temperature}}$$

In the presence of non-sucrose components a variety of methods¹ for expressing supersaturation may be defined. The ones commonly employed follow the above definition in terms of ratios and percentages, respectively; and regard the third component with respect to either sucrose or to the water.

That is, in ratio terms,

$$S = \frac{\text{sugar/water ratio in syrup}}{\text{sugar/water ratio in saturated syrup at the same temperature and purity}}$$

$$S'' = \frac{\text{sugar/water ratio in syrup}}{\text{sugar/water ratio in saturated syrup at the same temperature and impurity/water ratio}}$$

NAVEAU³ summarizes the various schemes in use for expressing supersaturation according to Table 1.

TABLE 1
DIFFERENT EXPRESSIONS FOR SUPERSATURATION (NAVEAU³)

KUCHARENKO	ratio	$\frac{\text{sugar/100 g solution}}{\text{sugar/100 g solution}}$	same purity
CLAASSEN	ratio	$\frac{\text{sugar/water}}{\text{sugar/water}}$	same temperature
VANHOOK	ratio	$\frac{\text{sugar/water}}{\text{sugar/water}}$	same purity
		$\frac{\text{sugar/water}}{\text{sugar/water}}$	and temperature
SILIN	difference	$\frac{\text{sugar/water} - 1}{\text{sugar/water}}$	same ratio
LANDT, VANHOOK and others	difference	$\ln \frac{\text{sugar/water}}{\text{sugar/water}}$	non-sucrose/water, and same temperature
SMOLENSKI	difference	$\frac{\text{sugar/100 g water} - \text{sugar/100 g}}{\text{activity solution}}$	same purity and temperature
Ideal theory	ratio	$\frac{\text{activity solution}}{\text{activity crystal}}$	same purity or same ratio sugar/water, and same temperature
	difference	$\ln \frac{\text{activity in solution}}{\text{activity crystal}}$	same ratio non-sugar/ water, same temperature
			same temperature

The International Commission for Uniform Methods of Sugar Analysis⁴ has approved the formulation in terms of sugar/water ratios at constant purity on account of long established practice even though the use of constant impurities has admitted theoretically advantages. The chief of these is the fact that during crystallization it remains constant, aside from any decomposition effects⁵. The question is discussed in a number of recent papers; notably those of SILIN⁶ and DUBOURG, SAUNIER and LEMAITRE⁷.

2. Methods

(a) *General*

Two general procedures are possible to determine the rate of growth of sucrose crystals suspended in a supersaturated syrup: either time to time observation of the dimensions of individual growing crystals or determination of the change in concentration of the medium. The former method is tedious but relatively free from any complications due to natural or induced nuclei generation. It is the method employed by most workers to ascertain the absolute speed of crystallization of sucrose. The second method is more convenient for studying the order and mechanism of growth. It gives true growth values only when developed in a comparative way.

(b) *Rate of Growth by Measurement of the Crystal*

Direct microscopic and projection measurements of the size of growing crystals or the determination of their weights have been used to ascertain the absolute crystallization rate of sucrose. The most extensive and consistent data obtained in this way are those of KUCHARENKO⁸ and co-workers. The results are presented in full in Section 3, p. 155ff. KUCHARENKO selected large (0.3 g), well formed crystals and grew them in a large excess of syrups of different concentrations and at various temperatures. Preheating of crystals, gentle agitation in a tumbling device at constant speed and adherence to many other operational details were necessary for reproducible results. The growing surface was computed from the relation

$$S^3 = CP^2$$

The constant C was assigned a value of 69.93 when P was expressed in g and S in cm². The stated value was ascertained by tedious measurements of the total surface and weights of 13 crystals ranging from 139 to 2500 g. The spread in values of C was from 63.2 to 76.0. The value of the shape factor is subject to the morphology of the crystals. Danish workers¹⁵ have recently pointed out that KUCHARENKO's value may be lower than that

characteristic of normal crystals; at least those obtained in commercial production. VANHOOK has the same matter under consideration in a program of reevaluation of KUCHARENKO's results. Most of the above workers confirm the general nature and relative validity of KUCHARENKO's results but intimate that his values may be high at the higher temperatures and stronger concentrations. This suspicion has been recorded in the recent reports of the crystallization Committee of I.C.U.M.S.A. and the matter in question is under investigation in several laboratories at this time.

Among direct methods for the rate of growth must be mentioned those based on the buoyancy of the crystal and incorporation of radioactive molecules. INGELMAN devised a HOOKE's balance apparatus but earlier used dilatometric methods²⁰. Most recently, GERASEMENKO and GOLOVIN²¹ describe a quartz filament balance with an accuracy of 10^{-5} , and with it determine the C.V. of sugar solutions at 70°, 80° and 90° C. ROBINSON²² outlines the determination of the speed of crystallization of sugar by means of tagged ^{14}C atoms.

(c) *Rate of Growth by Measurement of the Solution*

Several workers^{18, 20, 23-27} have studied the kinetics of sucrose crystallization in a relative way by means of the change in concentration of a supersaturated syrup in which crystal seeds are uniformly suspended. Although

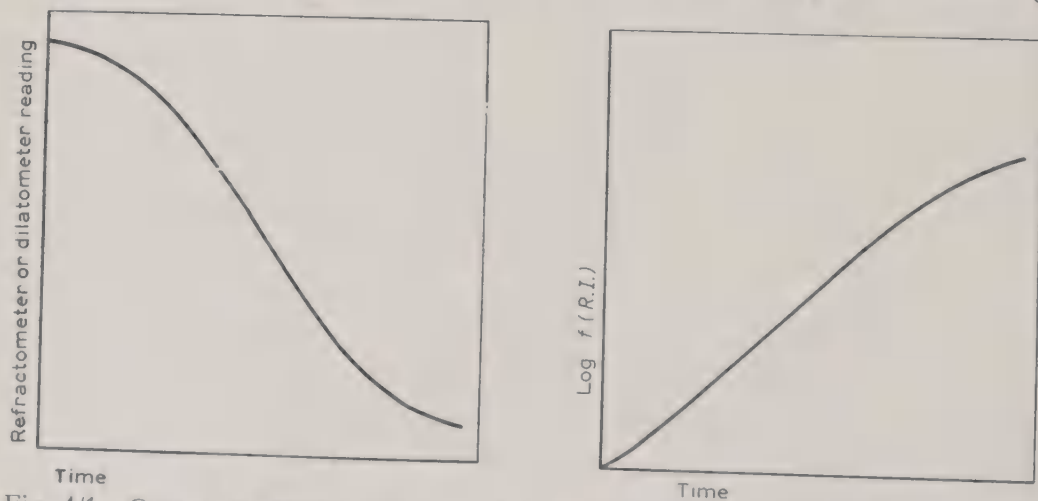


Fig. 4/1. Course of adjustment of a seeded, supersaturated sucrose solution, followed refractometrically^{23a} or dilatometrically²⁰ (schematic).

Fig. 4/2. Monomolecularity of crystallization velocity (schematic). The straight line, often extending from close to the beginning to as much as 3/4 life, suggests a unimolecular reaction in terms of supersaturation – or better, activities. The refractive indices may be converted to sucrose concentrations by means of a calibration curve²⁸ which is usually linear even in the presence of considerable concentrations of other components^{24, 29}.

any property dependent on concentration may be used for this purpose, the refractive index and density are most direct and convenient, especially since both may be ascertained on the unfiltered slurry if the grain density is not too great. The general type of result obtained in this way is illustrated in Fig. 4/1.

The S-like nature of the curve is typical of crystallizations and other autocatalytic processes. The three prominent sections of the curve have their proper counterparts in the kinetically more significant representation of Fig. 4/2. In this figure semilogarithmic coordinates are used and the middle linear portion emphasizes the unimolecular nature of the reaction according to the equation

$$V = k(C - C_{\text{sat}}.)$$

The induction period of the curve has been correlated with an area producing action^{23a, 25}, since it varies according to the amount and size of the seed used. It may be completely eliminated by the use of large amounts of very fine seed. The final diminishing part of the curve is due to the decreasing activity of sucrose in the solution and also partly to a decrease in surface available for growth as a result of agglomeration of crystals.

These explanations were tested in detail by VANHOOK and BRODEUR^{23c}. They considered the ever increasing area term when the seed density was limited, in which case the final integrated rate equation became

$$\log \frac{\sqrt{y_1^2 + y_1 y + y^2}}{y_1 - y} + \sqrt{3} \tan^{-1} \frac{2y + y_1}{\sqrt{3} y_1} = 4.12 kn^{1/3} y_1^2 t + \text{const.}$$

y and y_1 are simple functions of the concentrations at any time t and at saturation, and n is the seed density. This expression was tested graphically with the gratifying results represented in Fig. 4/3.

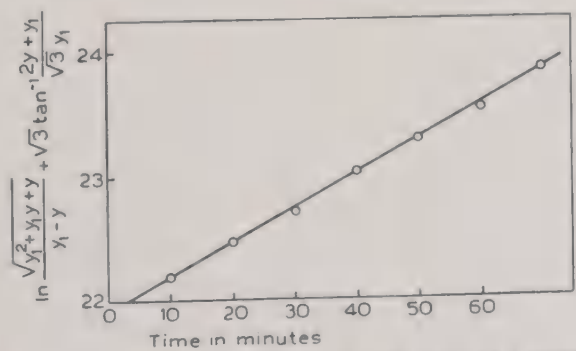


Fig. 4/3. Test of final equation with data of 1/400^{23c}.

(d) Experimental Variables

It is evident that the solubility of sucrose in the mother liquor is a most important parameter for kinetic considerations. This follows from the fact that the crystallizing potential is nothing but the concentration in excess of saturation. Solubility data in pure solutions are readily available³⁰, although even established tables are currently under investigation^{4, 31} on account of slight discrepancies.

KELLY has already discussed in detail the solubility of sucrose in impure solutions (Chapter 2). For any particular natural syrup there is often a definite solubility pattern, as exemplified by GRUT's table. In that case the kinetic analysis is considerably expedited. If the solubility is unknown, it must be determined. This may require a separate determination especially in single crystal work. In seeded experiments, the solubility may be connected with the end point of the crystallization. However, this determination may require extended periods of time even with pure syrups.

In VANHOOK's laboratory, for instance, it is observed that HERZFELD's solubility of 68.7% is consistently confirmed at 30° C by refractometer if the seed density is not high. This value is approached even after equilibration for several days. A slightly lower value is indicated in the same time period if the amount of crystalline material is increased considerably.

This difficulty is aggravated in the case of impure solutions and natural syrups; when the final adjustment occurs much more slowly than in pure syrups. It is our practice to increase the crystallization footings after the kinetic observations have been made, in order to accelerate the attainment of saturation. It may be visualized that addition of water to undersaturate, and subsequent equilibration to saturation with excess solid, might accomplish an improvement, since rate of solution near saturation is faster than the rate of growth. The impurity balance would be disturbed by this procedure.

It is also necessary, in growth experiments, that the habit of the crystallizing phase be known and remain constant during the determination. Ordinarily, this offers no difficulties, although minor variations have already been mentioned. POWERS has discussed these modifications in considerable detail in a previous chapter but a few additional remarks of kinetic significance may be pertinent. The most prominent example is that of raffinose in beetsugars. This promotes the formation of acicular forms³² according to the amount present. The effect on the velocity of growth has been considered in the GREAT WESTERN SUGAR CO. laboratories, and also by VANHOOK^{23a}. McCLEERY also reports the formation and development of needle

grain in cane juices high in gums and pectins. The crystals slow down the rate of boiling, frequently break in the pan and crystallizer, and tend to clog the centrifugal screens. Such complaints are not uncommon to the sugar boiler.

3. Rate of Growth in Pure Solutions

(a) Concentration

I.C.U.M.S.A.⁴ has recommended the adoption of KUCHARENKO's values of crystallization of sucrose from pure solutions as tentative standards until confirmed and extended. These data are available in a number of reference works in addition to the original source. They are summarized in Tables 2a and 2b and in Fig. 4/4. Table 2a and Fig. 4/4 represent smoothed values, as do most other reproductions, while Table 2b gives KUCHARENKO's particular determinations. WISE^{31a} has pointed out that the smoothing procedure gives an appearance and meaning which is not always evident from the original data.

It has already been pointed out that several workers have verified the general validity of KUCHARENKO's results, although it has been evident for some time that his results at higher temperatures and concentrations are probably too high. The data are also limited in that they fail to continue into the ranges of temperature and concentration employed in white sugar boiling. Some writers^{14, 34, 35, 36} complain about the diverging and inconsistent implications which arise from KUCHARENKO's results.

The set of curves displayed in Fig. 4/4 exhibits a pronounced curvature

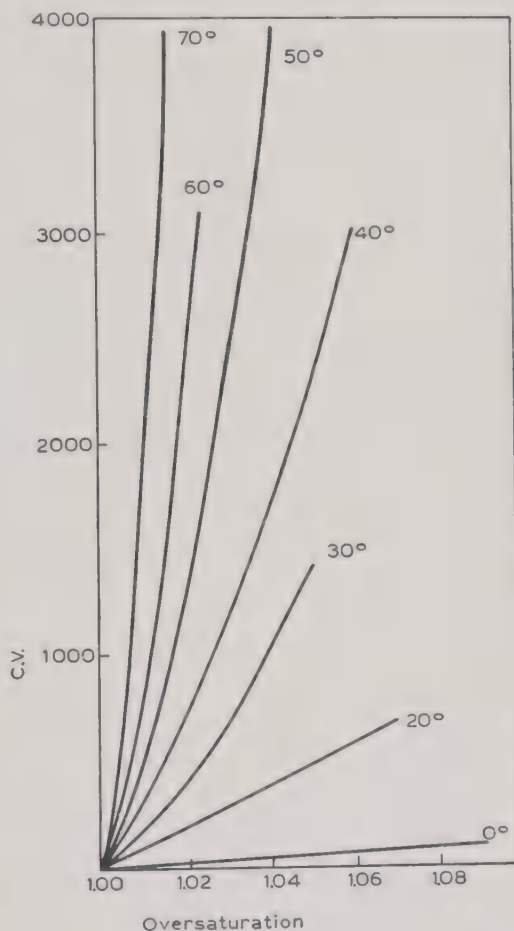


Fig. 4/4. Dependence between the velocity of crystallization and the oversaturation (% basis) of sucrose⁸.

which is reduced considerably if the supersaturation is expressed in some sort of a ratio concentration such as sugar/water ratio, molality, mole fraction, etc. This approach to linearity immediately suggests a growth equation of the form $V = k(S - 1)$.

The uncertainty which exists in the absolute value³⁰ of C_s leads to some

TABLE 2b
PARTICULAR VALUES⁸

°C	% Sucrose	C.V.	°C	% Sucrose	C.V.
0	65.57	9.8	50	72.91	431
	66.01	11.8		73.26	716
	66.79	20.1		73.69	1200
	67.74	29.3		74.17	1972
	70.19	54.6		74.76	2870
	71.17	75.4		75.51	4059
20	68.04	122.1	60	74.82	386
	68.38	141.7		75.10	953
	68.83	193.7		75.15	1017
	70.09	361.4		75.47	1839
	70.76	469.0		75.53	1881
	71.98	650.6		76.04	3098
30	69.50	188	70	76.90	1478
	70.01	369		77.18	2219
	70.41	495		77.36	2564
	70.57	552		77.51	3426
	71.28	829		77.55	3621
	71.84	1160		77.78	4138
40	72.31	1433		77.83	4191
	71.16	298.0		78.25	7259
	71.41	462.9			
	72.40	971.6			
	73.28	1575.5			
	73.91	2042.3			
	74.32	2618.1			
	74.59	2985.2			

variation when the supersaturation is expressed in this way, which difficulty may be circumvented by plotting velocity directly against concentration. KUCHARENKO's original data are presented in this way in Fig. 4/5.

Fig. 4/6 reassembles the same values on one plot and one scale. The large scale modulus develops only the salient features of the curves, essentially as straight lines. This is convenient and sufficient for comparative purposes. It is relevant to point out at this time that the indicated discontinuities appear between $S = 1.1$ and 1.2 at the lower temperatures while the breaks occur at slightly lower degrees of supersaturation at 60° and 70° C.

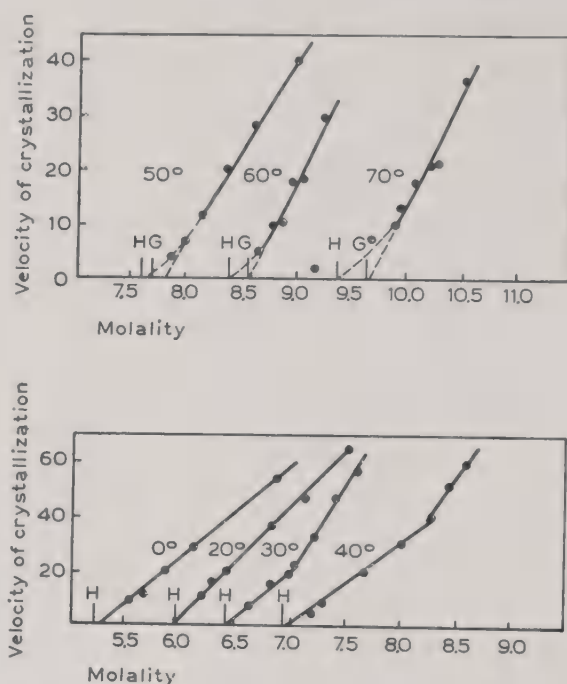


Fig. 4/5. KUCHARENKO's velocities of crystallization against molality. Solubility values of HERZFELD and GRUT marked H and G, respectively. Multiply velocity scale by following factors: 10 (20°), 20 (30°), 50 (40°), 100 (50° and 60°), 200 (70°)^{31a}.

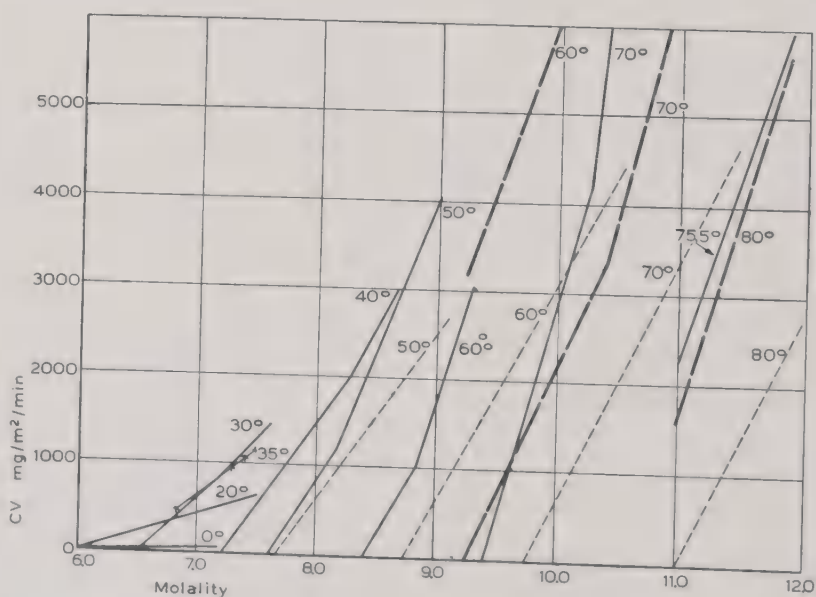


Fig. 4/6. Comparison of velocity data of several workers. — = KUCHARENKO⁸, ---- DE VRIES¹⁶, --- = DUBOURG and SAUNIER¹⁰, x—x = DOSS and GHOSH¹⁷.

The following list of papers and results will serve to appraise the validity of KUCHARENKO's results. The list is complete as far as the writer is aware. It is presented in chronological order.

(1) NAKHMANOVICH and ZELIKMAN¹⁸ confirm KUCHARENKO at 70° C, as given in Table 3.

TABLE 3

<i>S</i> (ratio)	<i>N</i> + <i>Z</i>	KUCHARENKO
1.03	1120	1300
1.06	2360	2200
1.09	4050	4000
1.12	6900	—

These workers report lower values than KUCHARENKO in a few experiments at other conditions but give no data. This is pointed out by SILIN³⁶.

(2) HONIG and ALEWIJN³⁹ confirm KUCHARENKO almost exactly at 20° and 40° C, and supersaturations (%) 1.025 and 1.050.

(3) DE VRIES¹⁶ determined the velocity of crystallization of sucrose from pure solutions at 50°, 60°, 70° and 80° C by the weighing method, and realized values considerably lower than KUCHARENKO. BREEDVELD and WATERMAN⁹ also observed the same, to even a greater extent, at 70° C. The patterns of their results are indicated on Fig. 4/6.

(4) AMAGASA²⁴ shows by a refractometric method that crystallization velocities at 30° are nicely linear in terms of ratio supersaturation when the seed area is large. It is not possible to orient his curve in the above plot, since growing areas were unspecified.

(5) THE GREAT WESTERN SUGAR CO. workers have measured the growth from pure solutions at 70° C by means of single crystal measurements. They also designate the transformation of linear measurements to KUCHARENKO units for both normal and non-normal growth. The comparison follows in Table 4.

TABLE 4
C.V. CALCULATED

Supersaturation in % terms	For normal growth	For non-normal growth	KUCHARENKO
1.010	480	635	1700
1.015	846, 807	982, 933	2665
1.020	1510, 1535	1720, 1750	4000

It is apparent, again, that KUCHARENKO's values are high.

(6) DUBOURG and SAUNIER¹⁰ measured the growth of sucrose crystals under the microscope at 10° intervals between 60 and 90° C. Their linear observations may be transformed to weight/area dimensions by means of the factors mentioned above in (5). The growth curves then assume the

approximate positions indicated in Fig. 4/6. The growth was considered to have been normal for this presentation. The non-normal factor increases the slope of the curves by approximately 15% but the elevated lines are still considerably below the corresponding ones of KUCHARENKO.

(7) INGELMAN²⁰ studied the crystallization of sucrose dilatometrically as

TABLE 5

S' by %	Rel. C.V.	KUCHARENKO (calc.)
1.020	1	1
1.027	1.38	1.41
1.034	1.81	1.87
1.041	2.43	2.39

well as by the increase in weight of a mass of crystals. It is not possible to convert his results directly to dimensions or weight per unit area increments, but a relative comparison reveals that KUCHARENKO's results are confirmed. INGELMAN worked at 25° C so that for comparison KUCHARENKO's values are interpolated to this temperature in a log C.V. - reciprocal temperature (°K) way.

This favorable comparison in the neighborhood of room temperature concurs with that of AMAGASA (4) and the experience of workers in the laboratory of the Holy Cross College^{23a}.

(8) DOSS and GHOSH¹⁷ have measured the displacements of the α -pinacoid faces of sugar crystals when growing in supersaturated syrups at 35° and 75.5° C. When their micrometer measurements are converted to KUCHARENKO units by means of the above mentioned factor the values are very much lower than those of KUCHARENKO's. The α -pinacoid dimension appears to be quite sensitive to conditions of growth. Preliminary investigations by MARTINOWSKY⁴⁰ in the Holy Cross College laboratory indicate that the conversion factor is better approximated by 1×10^6 than 0.491×10^6 . This factor transforms from mm/min to mg/m²/min and the larger one is used in the graphic comparison. This question of the factor of converting from linear to weight unit is being investigated further in the laboratory of the Holy Cross College under the auspices of the Sugar Research Foundation Inc. Future revision may alter the slope of the curves which have been drawn in Fig. 4/6; but current preliminary estimates indicate that the position relative to the KUCHARENKO lines will probably not be changed.

(9) Confirmation and extension of KUCHARENKO's data are being investigated in the Holy Cross College laboratory. Only preliminary reports^{23c, 23f} have been issued to date. They indicate essentially the same results at 20°,

(25°), 30° and 40° C, with good linearity out to about $S = 1.2$. This is slightly beyond the point of marked deviations in KUCHARENKO's curves. At 40° C our results begin to be less than KUCHARENKO's, amounting to about 20% at 9 molal.

The main conclusion of the above comparison is that KUCHARENKO's growth data are too high especially at high concentrations and elevated temperatures⁴. The correction cannot yet be specified quantitatively.

It has been pointed out previously that KUCHARENKO's growth data form a set of essentially linear curves when expressed in terms of supersaturation. However, a pronounced positive deviation appears in the latter portion^{23a}. This effect is magnified if KUCHARENKO's smoothed values are used in place of the original data.

WISE^{31a} has cautioned the interpretation under this circumstance and the question is under active reconsideration at this time. In the meantime, the analysis has progressed in the following way. Several explanations of an ever increasing crystallizing potential appear evident:

- (a) increased nucleation and induced grain at higher concentrations and temperatures,
- (b) accelerated growth as the result of strain or interruptions,
- (c) change in crystal morphology,
- (d) heat of crystallization,
- (e) increases in the activity of sucrose in solution

(a) is suggested by the correlation between the usual point of false grain formation and the appearance of the 'break' in a marked way in most of KUCHARENKO's curves. This suggestion may presumably be rejected on account of the technique employed and since KUCHARENKO mentions that measurements were discontinued when false grain appeared.

Strain does alter the rate of growth of crystals⁴¹. GRUT¹⁵ has pointed out that sucrose crystals assume steady growth rates only after considerable addition has occurred. This effect has been duly emphasized in work in the Holy Cross College laboratory. One of GRUT's typical experiments is illustrated in Fig. 4/7. It has also been observed^{23g} in the Holy Cross College

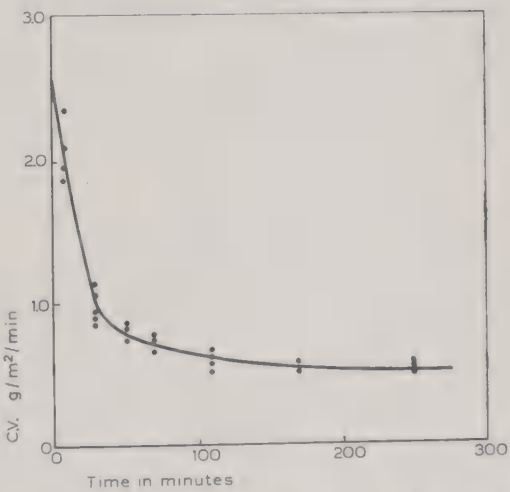


Fig. 4/7. Crystallization velocity of crystals altered by erosion and by partial dissolution as a function of time of growth¹⁵.

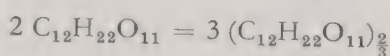
laboratory that the rate of growth of sucrose crystals can be accelerated as much as 50 % by means of thermal shock. Exposure to positive temperature gradients appears to be more effective than the reverse. It has also been observed in recent single crystal experiments in the Holy Cross College laboratory that growth rates are often altered drastically whenever minor interruptions in conditions occur. Similar effects have been reported^{42, 43} in other systems even when such disturbances are not apparent.

The rate of crystallization varies greatly from one crystal to another. BJERAGER⁴⁴ illustrated this vividly by means of photomicrographs of growing crystals and ascribes the differences to alterations in crystal habit. Minor habit differences are reflected in the variations of shape factors of KUCHARENKO's thirteen large crystals. It is imperative to specify the crystal form exactly when expressing growth data^{11, 12}.

As crystals grow faster more heat is generated per unit time. If this heat is not dissipated completely, and the effect of increasing temperature on reaction velocity is greater than on solubility (as appears probable), the speed of crystallization will increase. This possibility has been investigated^{23f} with the conclusion that even at rapid growth rates the heat of crystallization does not accumulate in ordinary experimental set ups.

VANHOOK^{23a} has advocated the last explanation but is currently reconsidering its theoretical implications in view of the recent valid criticism of WISE^{31a}. In the meantime the suggestion has been regarded with sufficient significance³ to justify a brief exposition here.

The alteration in the effective concentration of sucrose in solution as the result of hydration and tautomerism is reviewed by ORTH⁴⁵, CLAASSEN³⁷, and more recently by PEARCE and THOMAS⁴⁶. In effect, according to ORTH, equilibria of the type α -sucrose (solution) = β -sucrose (crystallizable) are established, and the β -form is favored at higher concentrations. He estimates from boiling point data that the corresponding molecular equation is:



At lower temperatures, freezing point data indicate a more nearly monomeric form of sucrose, according to ORTH. In view of the rather unsatisfactory significance of boiling point determinations⁴⁷, considerable doubt must be attached to the reality of this formula which suggests partial dissociation. The situation has been explained satisfactorily in both qualitative and quantitative fashions, and independent of any definite molecular form, in terms of the activity concept of the behavior of solutions^{23a}. This substitution of activity for molecular concentration was dictated by the general

success of the activity theory of solution kinetics^{48, 49} and the fact that the viscosity of the syrup may not be a primary factor in the rate of sucrose crystallization. For in that case a saturated film surrounding the growing crystal loses significance and in place of the corresponding saturation concentration there must be employed some property of the solid crystal itself which is identical with the same property of the saturated solution.

The activity, not the molecular concentration, is such a property and the usual growth equation:

$$\text{Vel.} = k(c - c_{\text{sat.}})$$

becomes

$$\text{Vel.} = k(a - a_{\text{sat.}})$$

The activity is, in effect, the concentration which must be employed instead of the real molecular concentration in order to validate the thermodynamic laws of solution. The relation between the two concentrations is defined by the activity coefficient

$$a = \gamma m$$

where

a = activity of the solute,

γ = activity coefficient,

m = molecular concentration, most appropriately expressed as molality.

The theoretical and experimental evaluation of this activity coefficient has been performed more extensively for electrolytes and for other solutes in the presence of electrolytes⁵⁰ than for non-electrolytes themselves⁵¹. No general behavior is found for these latter solutions, although empirically the activity coefficient may be represented in many cases by the theoretically acceptable type of equation:

$$\log \gamma = bm$$

where

γ = activity coefficient (of sucrose) at molality m ,

b = a constant.

The vapor pressure and boiling points of supersaturated sucrose solutions indicate the appropriateness of equations of this form. When these factors are put in the differential velocity equation the integrated result²³ describes the velocity of crystallization of sucrose fairly well.

The preliminary calculations are summarized graphically in Fig. 4/8. The first two are additional assemblies of KUCHARENKO's smoothed data in which log-log coordinates are used in order to compress the representation. The upward deviations at higher concentrations are evident in the first two figures, but the trend is apparently absent in the last.

DUNNING⁵² has published extensive values of the activity of sucrose solu-

tions whose use instead of the approximate estimates employed in the above preliminary computations confirms the applicability of the activity concept. However, WISE^{31a} criticizes some details of the analysis and also points out the inconsistencies arising from the use of smoothed data and supersaturations based upon HERZFELD's solubility tables. DOSS and GOSH¹⁷

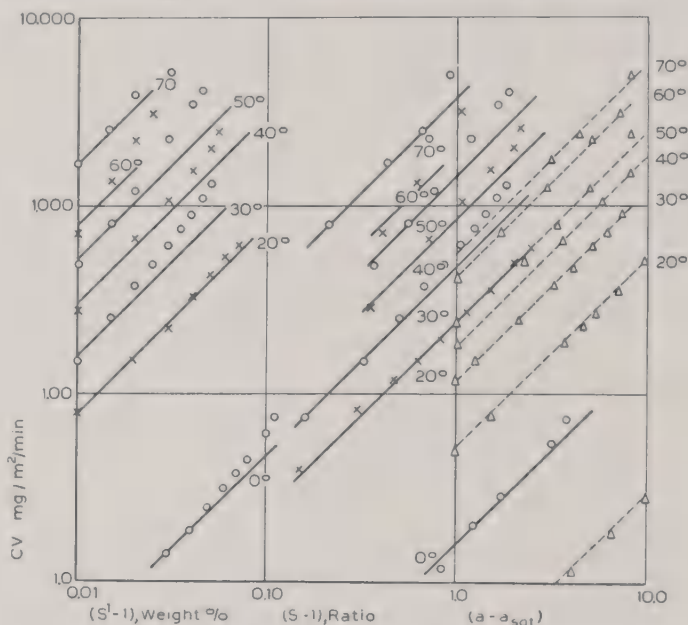


Fig. 4/8. KUCHARENKO's values for velocity *vs.* supersaturation in different units. The lines are drawn with slopes of 1 to indicate the unimolecularity^{23a}, corrected.

also remark that 'since activities and concentrations of sucrose are very nearly proportional to each other in the range of supersaturation (up to 1.15) studied in this work we cannot unequivocally conclude regarding their relative merits for correlating the growth rate'.

The high degree of uncertainty regarding the validity of KUCHARENKO's data at high concentrations and temperatures also serves to emphasize this conclusion. In view of this situation, the basic application of activities to pure sugar crystallization is under reconsideration in this laboratory and further reports should be following.

In the meantime, the suggestion has been well endorsed³ and is also successful in rationalizing the complexities of crystallization from impure solutions. This application is discussed in a following section.

(b) Temperatures

Temperature exerts a profound effect upon the crystallizing rate of pure sucrose syrups. The growth rate of solutions may either increase or decrease with rising temperature according to the concentration and the temperature.

A good part of this effect at different temperatures is due to the strong influence of this factor on the solubility. This complication may be eliminated from consideration for the time being by taking the slope of the early linear part of the curves in Fig. 4/6 as the specific reaction rate constant* according to the equation

$$V = k(c - c_s)$$

These rate constants are subject to the ARRHENIUS equation

$$k = k_0 e^{-\frac{E_{Act.}}{RT}}$$

where

- k_0 = a constant,
- $E_{Act.}$ = the activation energy associated with the process of growth.

Estimated values of k are plotted against reciprocal absolute temperature on a semilogarithmic scale in Fig. 4/9. 50° C is taken as the reference temperature in order to make the results of different workers comparable. The slopes of the curve decrease rapidly as the temperature increases and the corresponding activation energies fall from about 25 kcal/mole at 0° C to 1 kcal/mole in the 70°–90° C range.

These are activation energies computed according to the slopes of the linear growth equation $V = k(m - m_s)$, where the intercept is effectively the solubility. If the degree of supersaturation is introduced as $S = m/m_s$, the equation becomes $V = km_s (S - 1)$.

The corresponding ARRHENIUS equations are

$$k = k_0 e^{-\frac{\Delta H_m^*}{RT}} \text{ (constant crystallizing capacity)}$$

and

$$km_s = k_0 m_s^0 e^{-\frac{\Delta H_s^*}{RT}} \text{ (constant crystallizing potential)}$$

ΔH_m^* and ΔH_s^* represent activation energies at constant molality and constant supersaturation, respectively.

If the ratio of these is taken, $\frac{m_s}{m_s^0} = e^{+\frac{\Delta H_m^* - \Delta H_s^*}{RT}}$, in which m_s is the solubility coefficient with respect to a reference value m_s^0 . Ordinary solubility theory defines this as $e^{-\frac{\Delta H}{RT}}$; in which expression ΔH is the heat of solution. The difference in the two activation energies is then nothing

* This expedient eliminates the uncertainty attending still doubtful solubilities and supersolubilities. This latter approach was the one followed in an earlier analysis^{23a}; which computations also employed 30° C as the base reference temperature.

but the heat of crystallization. Being as this is an exothermal quantity for sucrose, it must be added to ΔH^*_m in order to yield ΔH^*_s . The heats of crystallization of sucrose are estimated from HERZFELD's solubilities to increase from approximately 1 kcal/mole at 20° C to 3.5 kcal/mole at 90° C.

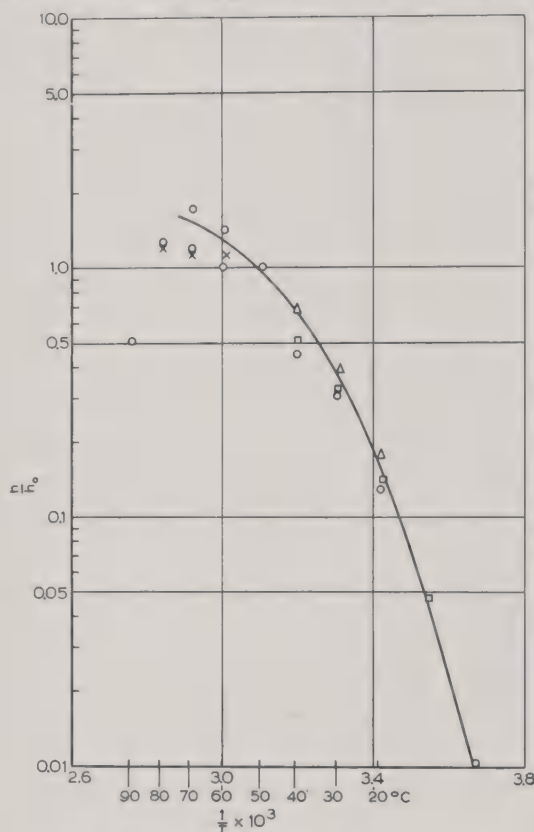


Fig. 4/9. Temperature coefficient of rate of crystallization. k_0 at 50° C. o = KUCHARENKO⁸, x = DE VRIES¹⁶, □ = VANHOOK *et al.* refractometer^{23a}, Δ = VANHOOK *et al.* single crystal measurements^{23g}, ○ = DUBOURG and SAUNIER¹⁰. k_0 at 60° C; k at 80° C = 1.25; k at 90° C = 0.53.

sucrose growth velocities by means of an elastic quartz filament. The velocity in pure solutions at 70° to 90° C increases linearly with the coefficient of supersaturation. The ten degree index is 1.25 from 70°–80° C and 1.3 from 80°–90° C. These correspond to energies of 5 and 7.5 kcal/mole, respectively.

The curve in Fig. 4/10 represents the manner in which the crystallization velocity depends upon temperature. However, this particular curve must be regarded as being provisional only. It is based upon widely divergent growth data, especially at the higher temperatures as well as solubility values which are subject to revision.

These are somewhat lower than observed^{23h} or calculated from improved data^{31b} but are to be used in transposing the above activation energies to the same tentative supersaturation basis. The activation energies at constant supersaturation become accordingly 26 kcal/mole at 0° C and 4.5 kcal/mole at 90° C. The complete change over this same range of temperature is given in Fig. 4/10.

This newly computed curve does not differ greatly from that previously reported^{23a}. The relative refractometric data of WHITTIER and GOULD²⁵ are estimated to parallel KUCHARENKO's values from 0° to 30° C, so that the activation energies would also concur. DOSS and GHOSH¹⁷ similarly report an activation energy of less than 5 kcal/mole from their micrometer determinations at 35° and 75.5° C. Most recently, GERASEMENKO and GOLOVIN²¹ report measurements of

(c) *Stirring*

Opinions differ concerning the influence of stirring and agitation upon the crystallization velocity of sucrose. Experiments on this question have lead different investigators to conclude that there is either a pronounced effect or relatively none—noncommittal decisions being relatively few. This situation immediately suggests that conditions and circumstances are not uniform and comparable, so that opposing conclusions are not necessarily contradictory.

In the English version of his works, KUCHARENKO states: ‘To judge of the dependence between the crystallization velocity and the velocity of rotation of the axis of the thermostat, we have not yet obtained the necessary data.’ All his experiments were conducted at the same speed of rotation.

On the positive side, SAVINOFF⁵³ found that the rate of crystallization of sucrose could be increased fivefold by stirring at 100 r.p.m., but that further increases were not realized above 400 r.p.m. AMAGASA²⁴ also reports that crystallization is increased by stirring and, accordingly, standardized his refractometric work at 15 r.p.m. DUBOURG and SAUNIER¹⁰ found that rapid versus no stirring tripled the rate of growth at 50° C.

The advantages of good circulation in pan boiling and crystallizing are evident^{54, 55} but do not necessarily signify enhanced speed of crystallization²³¹. CLAASSEN³⁷ questioned the practical utility of stirring in opposition to SPENGLER’s opinion⁵⁶. Recently DITMAR-JANSSE⁵⁷ claims that forced circulation is not necessary in pan boiling. The advantages of this arrangement are probably unique to the design and construction of individual pans⁵⁸. BIRCH-IENSEN⁵⁹ notes that agitation of massecuites becomes less important at low temperatures.

Also on the negative side, DE VRIES¹⁶ found that agitation had no appreciable effect on the crystallization velocity of sucrose at 70° C when constrained within the usual range of motion; but that an increase occurred when the motion of the crystal with respect to the liquor was rapid. SILIN

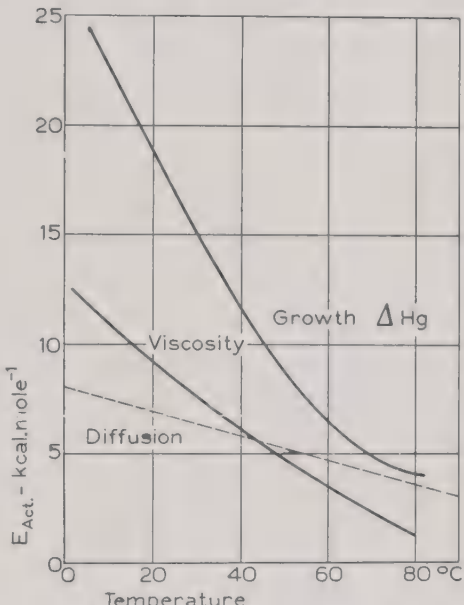


Fig. 4/10. Activation energies of growth, viscosity, and diffusion at constant supersaturation.

and SILINA³⁶ – strong advocates of the diffusion theory of growth – remark that slow stirring has no effect on the crystallization rate at 40° C. DAVIES and YEARWOOD⁶⁰ observe the growth velocity to be approximately doubled upon increasing the stirring rate from 1 to 5 r.p.m. but find virtually no further change at 25 r.p.m. ZHVIRBLYANSKI and coworkers state that stirring has no effect upon growth rates in the laboratory⁶¹, and GHOSH and DOSS note the same at 35° C over a range from 2 to 11.5 r.p.m.¹⁷. NAVEAU⁶² shows on crystallographic grounds that agitation should have no effect. HUNGERFORD's results⁶³ amount to less than a 10% increase in crystallization rate upon quadrupling the speed of his piston type stirrer.

VANHOOK's earliest experiments^{23a} indicated a dependence on the intensity of agitation, which, however, disappeared when the seed density was increased. Later single crystal trials at 70° C yielded similar results; namely, the effect at low stirring speeds diminished rapidly as the speed of rotation was increased. The empirical equation: $V = \alpha N^\beta$ represented the results, α and β being constants, and N the speed of rotation. The value of β varied considerably but was at most only 0.25 over the complete range from 0 to 3000 r.p.m. This limit of stirring frequency was later extended in investigations^{23j} on the effects of sonic and ultrasonic irradiations on crystallizing sugar syrups. At 8 kcycles/sec and 30° C, the increase in rate of deposition on single crystals was not greater than that accomplished by rotating the same crystal at 200 r.p.m.

In reviewing these various investigations on the effects of agitation, it seems to the writer that they have not extended over sufficient temperature, concentration, and stirring speed ranges. The partial results intimate that the effects are not drastic at ordinary temperatures and over protracted stirring conditions. These are significant patterns which pertain to the course of crystal growth and will be considered in the next section on mechanism of reaction.

(d) *Mechanism of Growth*

Impurities change the velocity of crystallization of sucrose from solution according to their kind and amounts. Combinations of different impurities are equivalent to natural cane and beet juices, so that this subject is one of paramount importance to the practice of sugar boiling. It is treated separately in detail in the following section. The question of the mechanism of growth is pertinent at this time.

The growth of a sucrose crystal within the body of supersaturated syrup obviously involves the transport of the units of construction to the growing surface and the accomodation of these units into the proper position in

the crystal lattice. If either of these two consecutive steps should be considerably slower than the other, the overall process will appear to proceed at essentially this same velocity.

The NOYES-WHITNEY-NERNST theory of reaction rates proposed that the transport operation dominated in heterogeneous reactions. In the case of dissolution or crystallization, a film of saturated solution would be established at the traveling interface, since adjustment within this zone would be prompt. The resulting rate of dissolution would be dictated by the rate of diffusion from this layer to the medium; and the reverse crystallization by an equivalent counter diffusion.

Satisfactory proof of the applicability of this diffusion layer theory was obtained from early experiments on the rates of solutions of metals in acids, interaction of metals and iodine, etc.⁴⁹; but later more critical work⁶⁴ was not as convincing. MARC's exhaustive studies on the velocity of crystallization from aqueous solutions⁶⁵ also demonstrated that the fluid film theory was not adequate in all instances. Later work⁶⁶ on many other systems confirmed that diffusion is not the universal controlling step in all crystallization processes.

(i) Diffusion

DEDEK³ has compared the rate at which sugar crystallizes to that at which it becomes available at the growing surface by diffusion. Table 6 is compiled from his computations at a fixed supersaturation of 1.05 g/cm³. The last row of figures suggests that excess sugar is available at the interface at low temperatures, but that this advantage is reversed above 50° C.

TABLE 6
CRYSTALLIZATION VERSUS DIFFUSION FOR SUCROSE³

Temp., °C	20	30	40	50	60	70	80
Sugar crystallized g/m ² /min	0.42	1.30	2.1	5.4	13.5	30	—
Sugar available by diffusion, g/m ² /min	10.8	5.9	5.2	2.8	1.6	1	—
Diffusion/crystall.	25.7	4.5	2.1	0.5	0.2	0.03	(0.002)

VANHOOK has reached essentially the same conclusion by comparing the activation energies of crystallization, diffusion, and viscosity^{23a, 23d}. In this respect these quantities are regarded as the energy barriers to the respective processes and therefore express the speed with which they take place. Lower values signify easier or faster reactions. These will have little influence on the net rate of reaction if the activation energy of a preceding or following

step is considerably greater. The comparison is presented in Fig. 4/10.

The energy of activation of diffusion is recalculated from the data of VANHOOK and RUSSELL^{23k}. These workers were unable to measure diffusivities of supersaturated syrups in their porous disc equipment, since the irregular surface induced crystallization and stoppage of flow. The highest concentrations for which diffusion coefficients were evaluated were still a few percents undersaturated at the 8.3° to 87.2° C range. Nonetheless, the data were extrapolated to a constant supersaturation of 1.05 (% basis) to estimate a linear activation energy curve which extended from about 5 kcal/mole at 20° C to zero at 55° C. In the present computation, the slopes of the log diffusion coefficient-reciprocal absolute temperature curves at the highest molar concentrations and extremes of temperature lead to activation energy extremes of 3 and 6 kcal/mole at the 90° and 10° C levels. The solution was 99% of saturation (% basis) in the former case, but only 85% in the latter. The activation energy at saturation and 10° C is probably higher by 1 or 2 kcal on account of the greater undersaturation⁶⁷. This estimated correction is included in the schematic curve in Fig. 4/10.

The approximate validity of this newly estimated curve is substantiated by the results of ENGLISH and DOLE⁶⁷. An interference fringe method was employed, and supersaturated solutions were studied to $S = 1.22$ at 25° C and $S = 1.13$ at 35° C. The lower limit of concentration was at 60 weight % or $S = 0.71$ and 0.66 at the two temperatures, respectively. Within these limits the activation energy of diffusion increased slightly from about 7 to slightly over 8.5 kcal/mole; or in round numbers 8 kcal/mole at saturation.

Only qualitative conclusions may be drawn from the diffusion and growth curves of Fig. 4/10. It is clear that the divergence is marked at low temperature but that the difference diminishes rapidly as the temperature increases. The provisional nature of the growth curve and the approximations involved in fixing its diffusional counterpart, allay quantitative estimates of the temperature at which diffusion begins to exert a profound influence on the growth rate. It is also necessary to recognize the possibility that only part of the integral diffusion coefficient may be significant in the operation under discussion, so that a complete elucidation of this question awaits the resolution of the diffusion coefficient into its many components⁶⁸.

(ii) *Viscosity*

The ordinary understanding that viscosity controls the crystallization of sugar^{8, 36, 69, 70, 71} implies the operation of a diffusional mechanism. The

relationship between the two is a reciprocal one, according to the STOKES-EINSTEIN function, but this has not been found to be exactly true for strong sugar solutions^{23k, 67}. The uncertainty in viscosity values in the supersaturated range and at higher temperatures may also modify their application in the present instance⁴.

In spite of these objections, VANHOOK^{23a} has compared the energies of activation of viscosity, diffusion, and growth, with the conclusion that the former two are considerably less than the third over the usual temperature range. The comparison was made at a constant supersaturation of 1.05 (% basis) and the three curves approach a common low level only at excessively high temperatures. The viscosity curve on Fig. 4/10 is recomputed on a ratio basis of supersaturation, according to the following considerations.

Fig. 4/11 is a semilogarithmic plot of viscosity against reciprocal absolute temperature. The data at $S = 1.0$ (saturation) are taken from PAYNE's compilation on p. 433 of Vol. I of this book. The other values are inter-

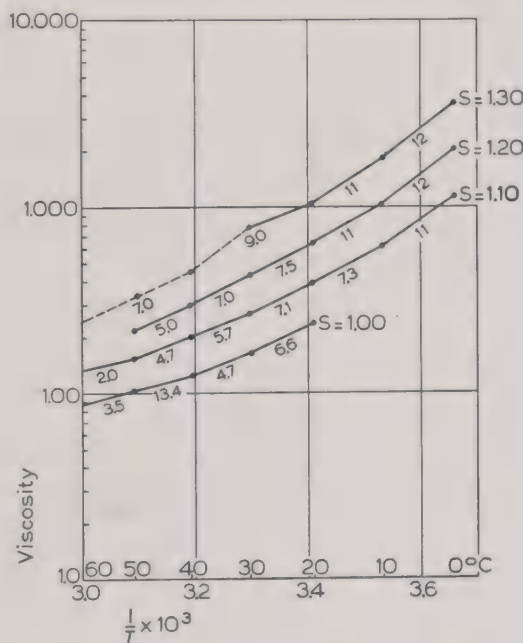


Fig. 4/11. Viscosity—temperature curves for pure sucrose solutions. $S = 1.00$ (see Vol. I, p. 433); $S = 1.1 - 1.3$ (see ref. ⁷²).

polated from LANDT's recent paper⁷² on the viscosity of pure sugar solutions. The numbers are activation energies calculated between the respective points.

The supersaturations are expressed with respect to HERZFELD's solubilities. When more recent, and probably more correct, solubilities are employed

the curves are essentially the same at preliminary temperatures but lead to smaller energies of activation at the higher temperatures (Table 7).

TABLE 7

ACTIVATION ENERGY AT SATURATION ACCORDING TO DIFFERENT SOLUBILITY DATA
(calculated from Vol. I, p. 433)

Temp. range, °C	HERZFELD	GRUT	TAYLOR
20-30	6.4 kcal	5.9 kcal	
30-40	4.7 "	4.4 "	
40-50	3.4 "	3.1 "	
50-60	3.5 "	2.6 "	0.5 kcal
60-70	1.8 "	0.7 "	0.2 "
70-80	1.2 "	-3.0 "	

It is also apparent (Fig. 4/11) that activation energies at a given temperature increase slightly with increasing concentration, so that the viscosity curve in Fig. 4/10 must be regarded as only very approximate. Together with the diffusion curve it displays a marked difference with the growth curve at low temperature; which deviations diminish as the temperature is increased. Plots, such as Fig. 4/11, for saturated beet juices at different purities reveal that the activation energies at 90 purity are approximately the same as white syrup; while at 80 purity and less (to 65) the values are much lower, and even relatively negative⁷⁰. This suggests that transport considerations do not dictate the growth rate at ordinary temperatures, but do become more significant as the temperature increases⁷³.

This inference cannot be regarded as unambiguous since many instances are known in which activation energies are not compatible with corresponding processes⁴⁹. There are, however, other qualitative indications that diffusion and viscosity do not play the dominant roles in the growth of sucrose from pure^{23a, 23b} and impure solutions^{35, 45, 74}.

(iii) *Added Colloids*

If a physical process was the rate controlling step in sucrose crystallization we would expect any agent increasing the viscosity to cause a decrease in the growth rate, and vice versa. This correlation is not observed in the case of added electrolytes²⁴ or invert sugar. The addition of the latter to a supersaturated solution decreases both the crystallization and the viscosity. Gum acacia^{20, 109}, dextran, pectins^{23d}, carboxy-menthyl cellulose¹⁷ and other colloids^{20, 109}, when added to syrups augment the viscosity tremen-

dously – even to the gelling point – yet have relatively little effect upon the crystallization velocity.

(iv) *Stirring*

The influence of agitation on the rate of heterogeneous reactions often reveals the course of their progress^{75, 76}.

It is generally recognized that reaction rate is a power function of the rate of stirring

$$K = \alpha N^\beta$$

where

K = velocity constant

N = rate of stirring

α & β = constants.

When the reaction is diffusion controlled β approaches unity, while otherwise β assumes zero or very low values. It has already been seen that β has values of only 0.25 or less for sugar crystals growing under normal conditions, so that it may be inferred that interfacial rather than transport factors prevail. However, it must be recognized that even this low value of the exponent varies considerably over the entire range of stirring speeds, so that the relative importance of these two steps will change accordingly. The influence of temperature is also incompletely known, so that the entire question is one requiring more detailed and outlined examination.

(v) *Crystallographic Considerations*

The fact that crystals preserve their habits when growing has been raised as an objection to the diffusion theory^{62, 66}. Since ordinary macro-diffusion is isotropic in space, the growing crystals should assume a spherical shape if only diffusion were important. This is not the case with sugar crystals under normal conditions of growth. On the other hand, this spherical form may be approached⁷⁷ in the partial dissolution of crystals. This and other evidence to be discussed presently suggests that the dissolution process is diffusion controlled. But it is also known that the ratio of the rate of solution of sucrose is greater than that of growth at equal degrees of under-saturation and oversaturation, respectively; so that the same mechanism is probably not operative in both cases.

An outstanding feature of the NERNST theory is the explicit formulation of the specific reaction rate constant in terms of D/δ ; where D is the diffusion coefficient and δ the effective thickness of the fluid film. The thickness

required in many heterogeneous reactions is usually about 20–40 μ , while DEDEK³ calculates 183 μ at 20° C, decreasing to 13 μ at 70° C for sugar solutions. While these dimensions are unrealistic, MOELWYN-HUGHES⁴⁹ considers the uniformity of size as consistent with a diffusion process.

(vi) *Summary*

It is impossible to draw any unassailable conclusions from the above discussion. The partial circumstantial evidence presented suggests to the writer that the transport step is relatively unimportant at low temperature, but that this interpretation is reversed at higher levels. The orientation and the diffusion processes appear to proceed at about an equal pace around 50° C. More extensive and detailed data on the rate of growth under these conditions are required to resolve the complicated kinetics of this dynamic process. The microscopic and supermicroscopic examinations initiated by POWERS (see Chap. 1) will be most useful in formulating a detailed account of the actual course of growth of sucrose crystals.

4. Impurities

(a) *General*

The variety and amounts of impurities that may be added to sugar solutions or to be found in natural syrups are almost without limit. The effects of these additional constituents on the crystallizing behavior of solutions are most important for theoretical and practical purposes. It would seem that a synthetic approach to the ultimate complexity of natural cane and beet syrups might have some advantages over an analytical advance by virtue of supplying more direct and specific information. For this purpose it is convenient to classify impurities as either electrolytic or non-electrolytic.

The electrolytic constituents are principally the soluble ash components of the natural juice; which, while variable in amount, typify the source material. The non-electrolytes are the non-sucrose sugars and the non-sugars. They are in part degradation and hydrolytic products of the original raw juice; together with natural gums, waxes, colloidal material, etc. Nitrogenous materials^{26, 80} are prominent in natural syrups and consist of a wide variety of solutes whose behavior extends from one extreme to the other on the polar scale. The outstanding non-sucrose sugars are invert in the case of cane products and raffinose in beet juices.

In general, all impurities impede the crystallization velocity of sucrose. Only few exceptions to this usual effect have been reported, and these are

small and pertain exclusively to electrolytes. DUBOURG and SAUNIER¹⁰, for instance, studied the effects of NaCl , CaCl_2 , and $\text{Ca}(\text{NO}_3)_2$ by direct microscopic measurements. While these salts depress the velocity in almost all cases, there are a few reversals at higher temperatures. KAUZNETZOV⁸¹ observed the effects of K_2CO_3 , Na_2CO_3 , $\text{Ca}(\text{NO}_3)_2$, CaCl_2 , and Ca aspartate and found that all but CaCl_2 retarded the crystallization, CaCl_2 actually accelerating it. This increase may be an electrolytic effect as discussed presently or it may be a complication connected with saccharate formation⁸².

KUCHARENKO⁸ observes CaO and Na_2CO_3 to retard the crystallization velocity of sucrose, while CaCl_2 has a positive, negative, or indifferent effect according to its concentration. AMAGASA²⁴ reports on NaCl , KCl , Na_2CO_3 , K_2CO_3 , Na_2SO_4 , Na and $\text{KC}_2\text{H}_3\text{O}_2$. He concludes that 'carbonates have the strongest retarding action on the crystallization of sucrose'. Chlorides and acetates follow in the order named. Na_2CO_3 shows an unusual behavior. K-salts in general have a greater retarding action than Na-salts. His results with $\text{NaC}_2\text{H}_3\text{O}_2$ show an acceleration up to about 1% added salt and thereafter a steady impeding action. AMAGASA was unable to correlate the velocity effects of added electrolytes with either the viscosity or solubility changes, but he did point out that some of the discontinuities occurred at approximately the same concentration as the inversion of the solubility coefficient. SUZUKI⁸³ has reported that traces of Mn- and Co-salts lower the viscosity of concentrated sugar syrups, shorten the evaporation and boiling times and thereby effect heat economies and reduce the rate of inversion. If true⁸⁴ 'some effort may well be expended to verify the findings of this investigator'⁸⁵. Other instances of beneficiation of sugar crystallization are described by MIRČEV and ŠANDERA⁸⁶, and by BRIEGHEL-MÜLLER⁸⁷. These also involve the addition of electrolytes to the strike. This unique situation is one of the factors which suggested the activity hypothesis which will be discussed presently.

No abnormal features appear to attend the addition of non-electrolytes to crystallizing sugar solutions. Of the materials known to occur widely in molasses, KUCHARENKO⁸ reports specifically the effects of caramel and D-glucose; SOMMER⁸⁸, AFFERMI⁸⁰ and GARINO⁸⁹ on amino acids and coloring matter. VANHOOK²³, and CAVALLARO and MANTOVANI²⁶ examine invert sugar, dextrose, levulose, nitrogenous compounds, and various other additives. ŠANDERA¹³, DEDEK⁹⁰, NAKHMANOVICH and ZELIKMAN¹⁸, and BIESELAER⁹¹, and others generalize by stating that organic substances slow up the speed of crystallization of sucrose.

The general pattern of rate decreasing with purity appears valid in the cases of natural cane and beet juices. The literature is much more abundant

on the crystallization velocity of sucrose from natural syrups than from synthetic syrups of specified constitution. In addition to being discussed in many of the papers already mentioned^{8, 10, 13, 14, 18, 27, 34, 42, 45, 81, 88, 90, 91, 92} the subject is treated exhaustively in many additional publications, chiefly with regard to sectional, seasonal, manipulative, etc. variations^{11, 12, 36, 42, 93-99}.

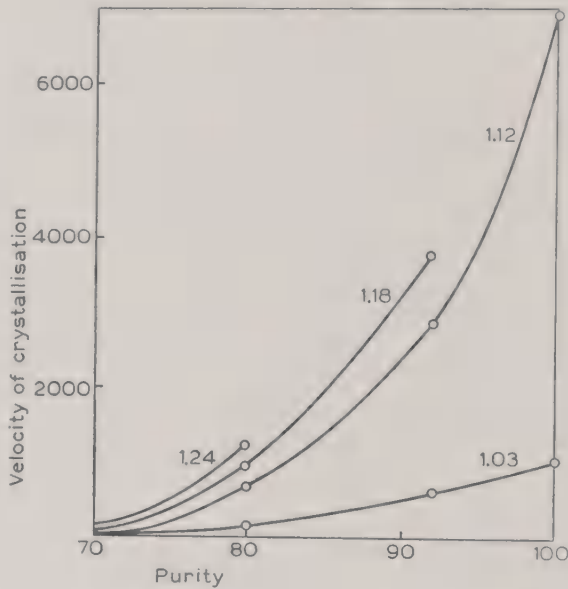


Fig. 4/12. Effect of purity on the crystallization velocity of sucrose¹⁸. The numbers on the curves are degrees of supersaturation.

While ‘the chemical differences in composition of (beet) juices which cause one syrup to be better than another (in crystallizability) are not known’¹¹ it is evident that the rate increases rapidly with increasing purity. For example; with a particular syrup the rate at 95% purity was approximately one-half that of pure sucrose, and at 80% purity one-ninth^{14, 97}.

Some representative data are given in Table 8 and Fig. 4/12.

TABLE 8
EFFECT OF DIFFERENT PURITIES ON THE CRYSTALLIZATION VELOCITY OF SUCROSE¹⁸

Purity	Degree of supersaturation							
	1.03	1.06	1.09	1.12	1.15	1.18	1.21	1.24
	C.V. in mg/m ² /min/70° C							
100	1120	2360	4050	6900	—	—	—	—
92	620	1540	2390	2850	3300	3750	4180	—
80	235	415	580	710	840	975	1105	1235
70	40	65	85	105	125	150	170	192

Bibliography p. 184-187

Although wide differences in absolute rates of crystallization of different syrups under identical conditions of temperature, supersaturation and purity exist, and also some slight variations in the general form of these curves¹¹, it is evident upon even casual inspection that the form presented in Fig. 4/12 is a general one. As discussed by NEES and HUNGERFORD¹²: 'Although the rates of crystallization from different syrups are not uniquely fixed by their purities, the general similarity of the pattern of the rate curves suggests the possibility that if we construct a family of curves for a representative syrup and then determine the rate for another syrup at a given purity, a new family of curves for the latter may be fairly accurately determined by transposition. This sort of transposition can hardly be defended except on the grounds of expediency'.

Before attempting to rationalize this pattern and the unique conditions pointed out above, the changes produced by the addition of different types of impurities may be summarized as follows.

Electrolytic impurities

- (1) The velocity of crystallization is diminished^{8,10,13,23,24}; higher concentrations being more effective¹³ but not proportionally so^{80,90}.
- (2) Similar salts have about the same effect at equal molal concentrations, and higher valent salts are more active¹³.
- (3) Hygroscopic salts are equally effective in reducing velocities¹³. Potassium salts seem to demand special considerations according to some investigators, and this may be associated with their non-hygroscopic nature.

Non-electrolytes

This type of impurity decreases the crystallizing speed of sucrose to a lesser degree as the amount increases.

Natural syrups

The pattern is the same as in the preceding case, with some uniformity of behavior for juices of the same kind and similarities in composition.

(b) *Activity Theory*

The solubility of sucrose in water is altered by the addition of a second solute; being most prominently either increased or decreased by different electrolytes². CaCl_2 displays both effects according to the concentration^{100, 101}. This same reversal is also reported for several other electrolytes by AMAGASA²⁴, and similar patterns are observed in the solubility-purity relationships of cane and beet molasses^{2, 102, 103}.

On the theoretical side, the solubility of a given substance in different

media may be represented by a constant activity of the saturating phase even though the usual solubility itself may vary. The former 'thermodynamic' and the latter 'molecular' concentrations are connected by the activity coefficient γ ; $a = \gamma m$. The solubility pattern of a particular substance may therefore be expressed in terms of the equivalent activity coefficient, γ .

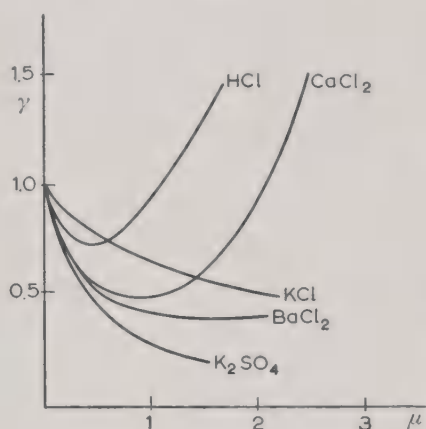


Fig. 4/13. Activity coefficients of electrolytes¹⁰⁴.

Activity coefficients of electrolytes display minima such as depicted in Fig. 4/13, while those of non-electrolytes usually vary monotonously with the first power of the concentration. The similarity between these patterns and the solubility relationships of sucrose described above first suggested the possibility of interpreting the crystallizing behavior of sugar solutions on the basis of an activity theory.

I. The hypothesis was originally applied to the case of pure sucrose solutions^{23a} and then to sucrose-salt^{23a} and other systems^{23d}. It is now realized that the first case needs critical reexamination in the light of more recent activity and growth data (*vide infra*)^{31c}.

In the case of impure solutions the activity theory starts with the reasonable assumptions of:

$$\log \gamma_1 = bm$$

$$\log \gamma_2 = \beta\mu$$

$$\log \gamma_3 = BM$$

The first definition refers to pure sucrose solutions, γ_1 = activity coefficient of sucrose in this state at concentration m (molal), b = a constant. The activity coefficient in the presence of electrolyte γ_2 is changed according to the amount of salt added, μ , the ionic strength, is defined as $\mu = \frac{1}{2} \sum m_i z_i^2$, where m = molality of each ion of charge z . Similarly, addition of non-electrolyte to the amount M molal changes the activity coefficient according to the third equation. β and B are constants.

The activity coefficient of sucrose in a solution at m molal, to which electrolyte to the extent μ has been added, will be: $\log \gamma = bm + \beta\mu$.

The rate of growth of sucrose from pure solution and from the same solution in the presence of electrolyte may be represented in activity terms by the equations

$$\begin{aligned} V_{\text{pure}} &= k(a_{\text{pure}} - a_{\text{sat.}}) \\ V_{\text{imp.}} &= k(a_{\text{imp.}} - a_{\text{sat.}}) \end{aligned}$$

The fact that pure sucrose of the same activity crystallizes out in each case is recognized in the difference of these two equations, namely

$$V_{\text{pure}} - V_{\text{imp.}} = k(a_{\text{pure}} - a_{\text{imp.}}) = km e^{bm}(1 - e^{\beta\mu})$$

This difference equation is not as advantageous as the ratio

$$\frac{V_{\text{imp.}}}{V_{\text{pure}}} = \frac{a_{\text{imp.}} - a_{\text{sat.}}}{a_{\text{pure}} - a_{\text{sat.}}}$$

If the gross approximation is made that the common activity at saturation is small compared to that in the actual solutions of the same sucrose molality;

$$\begin{aligned} \text{Rel. } V &= \frac{a_{\text{imp.}}}{a_{\text{pure}}} = \frac{\gamma_{\text{imp.}}}{\gamma_{\text{pure}}} \\ \log \text{Rel. } V &= \beta\mu \end{aligned}$$

The data of AMAGASA (Fig. 4/14) are seen to comply roughly with this equation; except for sodium sulfate which he mentions as being unusual.

II. VANHOOK^{23a} has also tested this equation with a wide variety of salts. While exact agreement is not found, it is gratifying to observe an approximate linear pattern especially as the powerful valence factor

is featured. A more detailed analysis of the nature of the β factor, based on the DEBYE-HÜCKEL theory of electrolytic interaction, revealed the requirement of an initial increase in growth at low salt concentrations, and this was also observed^{23a, 23d}.

III. The combination of sucrose and non-electrolyte is similar to the above case with the final equation being

$$\log \text{Rel. } V = BM$$

The approximate linear pattern on a semi-logarithmic plot of a wide variety of such additives to a considerable concentration is illustrated in Fig. 4/15.

IV. The case of sucrose-salt-non-sucrose is of special interest, since this

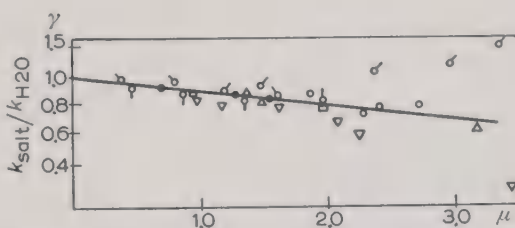


Fig. 4/14. Effect of electrolytes on velocity constant at 30° C. Data of AMAGASA^{23a, 23d}.
 $\circ$ = NaCl, $\square$ = KCl, $\triangle$ = Na₂SO₄, ∇ = K₂CO₃,
 $\diamond$ = Na₂SO₄, $\odot$ = NaC₂H₃O₂,
 $\odot$ = KC₂H₃O₂.

combination is equivalent to natural juices. The equation for the activity coefficient of sucrose in such solutions is:

$$\log \gamma = bm + \beta\mu + BM$$

The velocity with which sucrose forms from this solution relative to the

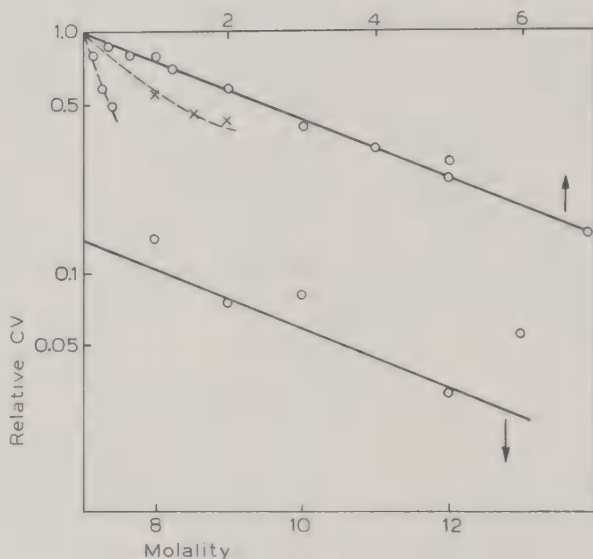


Fig. 4/15. Effect of non-electrolytes on the crystallization velocity of sucrose. — = invert sugar and its separate components: phenol, aniline, ethyl alcohol, etc.; the circles are typical experimental points. -- x -- = betaine; — o — raffinose. See. ref ^{23d}.

rate from pure solution at the same sucrose molality will be

$$\log \text{Rel. } V = \beta\mu + BM$$

Since the ratio of impurities remains fixed for any real juice, aside from decomposition, we may combine the impurity terms and write this equation as

$$\log \text{Rel. } V = iI$$

where

I = concentration of impurities,

i = a factor expressing their effect upon the crystallizing potential of sucrose.

VANHOOK at first designated this term a melassigenic factor, but now considers BRIEGHEL-MÜLLER's suggestion of retardation factor as more appropriate¹⁰⁵.

Fig. 4/16 illustrates the behavior of several representative natural juices according to this proposition. The agreement in these and similar cases is again not perfect, but the pattern of approximately straight lines is generally typical. This has suggested a method for evaluating the crystallizing qualities of different sugar house liquors according to their i values⁴.

(c) *Factory Work*

The ultimate purpose of crystal growth theories, in so far as practical considerations are concerned, is the understanding and improvement of operations at the pan and crystallizer stations. Some speculations in these di-

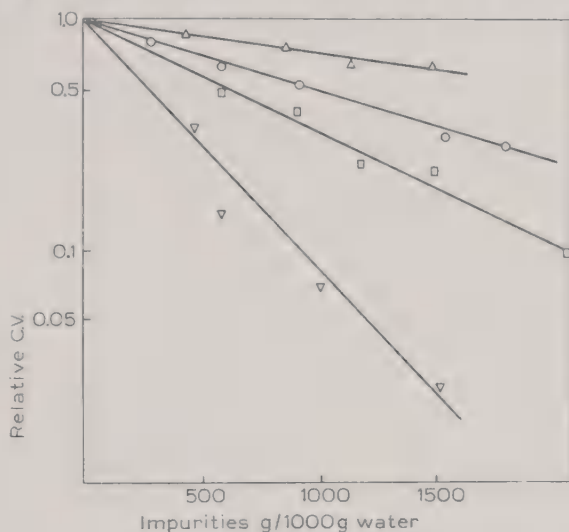


Fig. 4/16. Relative crystallization velocity of typical sugar house syrups. (If a molecular weight of 200 is assigned arbitrarily to the molasses constituent, these curves are comparable to those of Fig. 4/14 and 4/15^{23d}).

rections have been made^{23b, 231, 231} but only two additional will be offered here.

The retardation factor i has already been defined as the proportionality factor between crystallization velocity and concentration of impurity in natural syrups. Should the explicit formulation suggested prove to be inexact, it seems likely that some similar intensity factor would express the character of the melassigenic components of natural syrups. It would then remain to evaluate the functional dependence of this quantity on the concentration. The appropriate thermodynamic procedure is available⁶², only more extensive and detailed data are required. In the meantime, the simple semilogarithmic relation is being investigated and exploited⁴.

It has been found empirically that the optimum operating condition in crystallizers is realized at constant supersaturation of the mother liquor^{231, 106, 107}. In this instance we may regard the velocity of growth V as being determined chiefly by the crystal area A and the supersaturation S ; namely $V = kAS$.

This expression will have a maximum value in time when

$$\frac{dV}{dt} = kS \frac{dA}{dt} + kA \frac{dS}{dt} = 0$$

Now, the weight of crystals is proportional to their diameter cubed while the area is proportional only to the square. The weight is then proportional to the $3/2$ power of the area. The increase in weight with time, dw/dt , which is also the decrease in supersaturation, $-dS/dt$, is then proportional to $A^{1/2} \frac{dA}{dt}$. Inserting this term in the above condition for an extreme

$$S_{\max.} = \text{const. } A^{1.5}$$

If no false grain is forming, and since the area of the relatively large crystals is changing only slowly, we have the conclusion that the optimum cooling rate is one which maintains a relatively constant supersaturation¹²¹. A similar conclusion results from consideration of purity changes¹⁰⁸.

5. Dissolution

The dissolution of sucrose in water is presumed to be a diffusion controlled process. However, the process is not isotropic, as demanded by the NOYES-WHITNEY-NERNST rule, since the different faces dissolve at different rates⁶⁶. This is immediately evident from the etch-figures presented by PHELPS¹⁰⁷. Those on the left, truncated, prism faces are aligned along the central b -axis of the crystal, while the etch-figures on the right end prisms are normal to this axis. The faces are not equivalent crystallographically^{109,110}!

KUCHARENKO⁸ measured the rate of dissolution of sucrose crystals in almost saturated solution at 60°C . In expressing the results he does not use the same rate units as in his growth determinations because the surface of the crystal became engraved during solution. By assuming the same shape factor (4.12) for both processes, Table 9 is assembled from KUCHARENKO's data.

TABLE 9
KUCHARENKO'S SOLUTION AND CRYSTALLIZATION VELOCITIES

Coeff. of supersaturation (% basis)	Solution velocity	Crystallization velocity
0.9896	4800	720
0.9813	8620	1980
0.9754	14500	3000

The crystallization velocities are five or more times the solution rate at equal displacements from saturation, whether the supersaturations are expressed on a percentage or ratio basis.

HUNGERFORD¹¹ suggests that the difference may be explained in three ways:

(1) Nearly seven times as much surface is exposed due to engraving of faces. This is exceedingly unlikely.

(2) The viscosity is sufficiently lower to permit more rapid diffusion of sugar away from the crystal. It can be shown that this, too, is unlikely if not impossible.

(3) Deposition of molecules on a crystal involves some time consuming orientation which is not required in the process of solution from a crystal.

KUCHARENKO emphasized the role of the etched surface and in a separate experiment at 20° C determined the rate of growth of crystals whose surfaces had been enhanced by partial dissolution. At coefficients of supersaturation of 1.025 such crystals grew at first about twice as fast as after growth had proceeded for some time. GRUT³ found a ratio of 3 to 4 at 40° C and $S = 1.06$. If these differences are taken into consideration, the ratio of solution to crystallization velocity still remains at least 2 to 1. This is approximately the same as found by VANHOOK^{23b} when comparing the two processes with 75 purity cane and beet molasses at 6% displacements from saturation at 30° C.

This ratio disfavors the role of diffusion in growth in contrast to its operation in the solution process, but the margin of preference is not large nor is it well defined with respect to temperature and concentration. This is one more question that warrants further experimental investigation; the results of which should pertain directly to a clearer understanding of the mechanism of growth and dissolution^{109, 111}.

ŠANDERA¹³ has used the diffusion theory of solution to account for the rate at which sucrose crystals dissolve in water. The speed of solution R is directly proportional to the weight m of sugar and inversely proportional to the surface p and time t

$$R = \frac{m}{pt}$$

Since the surface p is directly proportional to the 2/3 power of the weight

$$R = \frac{K}{t} m^{\frac{1}{3}}$$

where K = shape factor of 0.203 common to the normal sucrose crystal. This equation was found to fit the observations satisfactorily. The influence of temperature was studied later¹³, and from the simple relationship: $k_t = 0.05t$ one computes a 10° C coefficient of 1.33 in the 30° range. Here,

k_i is a specific reaction rate constant at t° C. The coefficient corresponds to an activation energy of 5.7 kcal/mole, which value is agreeable to a diffusional mechanism.

Dissolution considerations are applicable in the affining of raw sugars, pan boiling^{91, 92, 112, 113}, treatment in the crystallizers, washing in the centrifuges, and in the recrystallization which occurs in the fabrication of cubed sugar¹¹⁴ as well as in the caking of crystals¹⁰⁹. On the experimental side, HUDSON¹¹⁵ has employed the method of maximum solution velocity to resolve the isomeric composition of many sugars. KAGANOV¹¹⁶ finds that the rate of solution of $K_3Fe(CN)_6$ in sugar solutions undergoes a marked change above 19% water content. This point corresponds to a molar sugar/water ratio of 4.5, which is just about the accepted degree of hydration of sucrose in water.

The viscosity of massecuites is especially important in crystallizer and centrifugal work. There is a minimum for optimum operating efficiency which may be attained either by dilution or heating^{109, 117, 118, 119}. The latter operation is found by practical experience to be the more effective. But some water is required for washing, and the possibility of dissolving crystals becomes significant. The more viscous a molasses, the slower is the rate of elimination, and the greater the quantity of wash water needed to free the crystals from adhering molasses. The net result is usually a crystal with a dilute molasses layer. 'Such a sugar will not keep well although its factor of safety may be satisfactory'¹²⁰.

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CHAPTER 5

CHEMISTRY OF CRYSTALLIZATION

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1. Introduction

The chemistry of the boiling process has many aspects which we should differentiate for a good understanding of the technical crystallization of sucrose.

The main features in this process are:

- (a) decomposition of sucrose, specifically inversion;
- (b) decomposition, transformation and condensation reactions of reducing sugars;
- (c) decomposition and transformation, the precipitation and coagulation of organic nonsugars;
- (d) phenomena related with the solubility of different types of inorganic nonsugars;
- (e) nonsugars affecting the crystallization of sucrose;
- (f) phenomena related with the dissolution and regrowth of sucrose crystals;
- (g) effect of precipitated nonsugars on the purity of the centrifuged sugar.

A part of these phenomena does not belong, strictly speaking, to the field of chemical knowledge¹. Some belong more to a specialized field of physics or physical chemistry; for instance, the inclusion of mother liquor in sucrose crystals. The accumulation of finely suspended or precipitated nonsugars in the mother liquor and the separation with the sucrose crystals from the mother liquor by the centrifugal process belong to a subject of chemical engineering: filtration.

It is necessary that the reactions and observations to be made in connection with sucrose crystallization are distinguished in different paragraphs thereby obtaining a proper understanding of what is actually taking place

in the crystallization and recovery of sucrose as a commercial product either as raw sugar or refined sugar.

2. Decomposition of Sucrose during the Crystallization Process

The main conditions in the inversion rate of sucrose are primarily the temperature and pH of the mother liquor. Once sucrose has been obtained in a crystalline form, the sucrose under the normal conditions of processing in pans, crystallizing, drying and screening, and later on during storage as a solid product, does not show marked changes in the interior of the crystals. Experiments, made by keeping sucrose crystals at temperatures of 70°C for a longer time (2 to 3 months), did show that the interior of the crystals remained practically unchanged with no formation of coloring material and no break down of the sucrose molecules into reducing sugars.

A sucrose crystal, once it has been formed, has a great stability at temperatures under 70°C , and does not show any remarkable changes in chemical composition or in its crystal characteristics. The same stability is not found for the traces of mother liquor or solutions surrounding the crystals. This is a material of much lesser stability. When a technical sugar product is kept in a closed bottle at a temperature of 70°C for several days, respectively weeks, it can be observed that there is an increase in the color of the sugar, but concentrated on the outside of the sucrose crystals. Also a certain amount of decomposition of the reducing sugars can be observed, respectively an increase in the reducing sugars content depending on the moisture content of the surrounding film of solution.

These changes in the composition and the aspect of white sugars can be used in testing different types of sugar on the stability during storage. A correlation can be found between the changes in stored sugar over a longer period of time and the changes observed by keeping sugar samples during 1, 2 and 3 days in an incubator at 70°C .

The first rule in studying decomposition and changes in the composition of massecuites during the crystallization process is that we have to consider the composition of the mother liquor primarily.

The stability of sucrose in solutions to a brix of 60 in relation to pH and temperature has been investigated carefully. The inversion of sucrose in technical sugar solutions 50 to 100 purity and a temperature range from $30\text{--}100^{\circ}\text{C}$ depends primarily on pH, temperature and time. The amount of sucrose destroyed by inversion is proportional to the time. The relationship between pH and temperature and the rate of inversion have been given in Volume I, pages 447 and 589. The stability of sucrose at the con-

centrations as found in the crystallization process at a brix level, depending on the purity, of 78 to 90 and a temperature range in pans from 60–75° C and in crystallizers from 30–70° C, has been studied in a few isolated cases and not always under well controlled conditions. The interrelationship between the inversion of sucrose and the transformation of the reducing sugars under the same conditions is not exactly known.

Some experiments with high purity solutions in a purity range of 95 to 100 were made as a preliminary investigation at the Java Sugar Experiment Station between 1930 and 1935.

One of the difficulties in this study is the consideration of the actual pH of the studied concentrated sugar liquors. When a concentrated sugar solution is diluted, there is a dilution effect on the measured pH-value as determined with hydrogen -chinhydron- and glass-electrode. A slight increase in pH is obtained with the dilution of a concentrated sugar solution. The determination of the pH at concentrations of 75 brix gives a certain value for the pH, calculated under the assumption that the rules applicable for diluted solutions are valid for concentrated sugar solutions. This is not absolutely true; the phenomena we are confronted with are more complicated in concentrated solutions. To find a correct value for the pH of solutions between 75 and 85 brix is a complex physical chemical problem; we are not yet able to give a clear picture of what has to be understood by the pH or the H-ion concentration of this type of solutions.

We can bypass these difficulties by introducing a standard technique for expressing the pH of the studied concentrated solutions. As simplification we can use the determination of the pH of the sugar solutions, diluted 1 : 1, measured at laboratory temperature, or with a glass-electrode measured at the same temperature as the decomposition reaction of sucrose is studied. This is the way this investigation was conducted at the Java Sugar Experiment Station.

The decomposition of sucrose by inversion, determined via the amount of formed reducing sugars, was in concentrated solutions higher than it was found for diluted sugar solutions to 65 brix. In high concentrations (75 brix and higher) the loss of sucrose by inversion was approximately double of what had been calculated as the inversion losses by the application of the STADLER tables.

Table 1 gives a number of data on the decomposition of sucrose per hour, derived by interpolation from a limited number of determinations. At present it has become possible to study this inversion reaction in low purity products in detail by the development of new analytical techniques, specifically the methods of chromatography. We are able to determine the

TABLE 1

Inversion of sucrose in % per hour in solutions of 75 brix in relation to pH, determined with H-electrode at room temperature, in dilution 1 : 1 (pH adjusted with H ₃ PO ₄ and NaOH). Solutions of high grade refinery liquor; ash content 0.06%, reducing sugars 0.08%.					Mixture of carbonation cane syrup + refinery liquor, purity 94.5 (pH adjusted with NaHSO ₃ and NaOH ⁹)					Inversion of sucrose per hour, calculated according to the STADLER tables				
Temp. °C	pH				Temp. °C	pH				Temp. °C	pH			
	5.5	6.0	6.5	7.0		5.5	6.0	6.5	7.0		5.5	6.0	6.5	7.0
60	0.02	0.005	—	—	60	0.04	0.01	—	60	0.011	0.0035	0.0011	0.0004	0.0001
65	0.03	0.01	± 0.004	—	65	0.06	0.02	—	65	0.023	0.07	0.0023	0.0008	0.0002
70	0.05	0.02	± 0.006	0.002	70	0.10	0.04	0.01	70	0.035	0.011	0.0035	0.0011	0.0003
75	0.09	0.05	0.02	0.01	75	0.15	0.08	0.04	75	0.070	0.022	0.007	0.0002	0.0006

individual decomposition products, levulose and dextrose, and to obtain a better understanding of this reaction.

The inversion reaction has great significance for practical sugar manufacture. In sugar factories manufacturing direct white sugars, it is customary to apply sulfitation of the syrups. The system to control the intensity of the sulfitation process is based on either titration of the amount of added SO_2 with iodine or it is checked by a determination of the pH of the sulfured syrups.

With the last mentioned system of control it must be understood that the pH of a syrup is not identical with the pH of the syrup after it has been concentrated in the vacuum pans for crystallization; a part of the SO_2 is eliminated from the syrup under vacuum. It is found that when a syrup has been sulfured to a low pH, as done occasionally in canesugar factories manufacturing sulfitation white sugar, the pH of the concentrated syrup is substantially higher than that of the original sulfured syrup. The pH of the mother liquor after dilution to the same brix as the original syrup shows a higher pH than the original material. These changes in pH are demonstrated by the data given in Table 2.

TABLE 2

pH OF SUGAR HOUSE PRODUCTS DETERMINED AT DIFFERENT CONCENTRATIONS AT ROOM TEMPERATURE WITH GLASS-ELECTRODE

		brix			
		60	70	75	80
Raw sugar	97.0 pol	6.7	6.5	—	—
Syrup	84.0 purity	6.7	6.6	6.5	6.4
A-molasses	70.2 purity	6.5	—	6.3	—
B-molasses	51.0 purity	6.4	—	6.2	6.0
Final molasses		6.2	—	6.0	5.8
Effect of concentration on pH of sulfured syrup					
after sulfitation brix 64.0	after concentration in vacuum pan to 68 brix	after concentration in vacuum pan to 74 brix	after dilution of 74 brix syrup to 37 brix		
Sulfured syrup 5.5	6.1	6.2	6.4		

The pH of syrup, specifically in the application of sulfitation, is no indication of the pH existing in syrup boilings or A-masseccutes. It is not permissible to use the pH of sulfitated syrups as a foundation for the calculation of eventual inversion losses. The inversion losses in the crystallization process must be based on the pH of the mother liquors in the masseccutes in the different stages of crystallization.

Practical questions that come up regularly are: What are the actual sucrose losses in the crystallization process from syrup to final molasses in raw sugar mills? Is there a solid foundation to estimate these losses as being more or less inevitable as a result of normal operational conditions?

To answer these questions, we have to start with the realization that the pH of the different types of massecuite is determined via a dilution technique differing from the real value of the pH at the concentration of processing, but which must be accepted as long as we have no ways and means for the determination of the real pH.

The pH of massecuites in canesugar mills can show, according to our experience, considerable variations depending on the pH of the clarified juice, the system of clarification (specifically liming), sulfitation of syrups, and refining methods, resulting in different pH-levels of the liquors after purification.

The pH of the mother liquor in *A*-boilings (purity 80–85) can vary, determined in dilution 1 : 1 and analyzed at laboratory temperature, from 5.8 to 6.8, for *B*-massecuites from 5.6 to 6.5, and for *C*-massecuites from 5.5 to 6.4. Determined as averages there is a slight decrease in the pH of the molasses with decrease in purity. For refined sugar strikes in actual practice, considerable variations can be found. The greatest stability and uniformity in the pH are found in bonechar refineries, where the pH of the first liquor is between 6.9 and 7.1. The first refined sugar strikes have usually a pH 0.1 to 0.2 points lower than the pH of the liquor. But in the refining with vegetable carbons combined with fosfatation or with other types of purification technique, it is occasionally found that the decolorized liquor going to the pan floor has a pH fluctuating between 6.4 and 7.4.

Some factories have the tendency, probably for good reasons, to purify and decolorize on the acid side. Other refineries favor neutral conditions in processing liquors. With vegetable carbon refined liquors, the decrease in pH from liquor to first massecuite can be as high as 0.3 to 0.4 pH unit.

In discussions on sucrose losses, the main factor in the inversion of sucrose is the pH and secondly, the temperature of processing. It is for this reason not possible to give as a general statement a quantitative expression for the sucrose losses in the crystallization process.

We consider that in raw sugar mills under ideal conditions, the sucrose losses from syrup to commercial sugar and final molasses are of the magnitude of 0.4% of sucrose in syrup. This is an inevitable loss. We have no ways and means at our disposal to reduce these losses because they are the natural result of the composition and our applied systems of crystallization.

Indications exist that under exceptional conditions with a low pH-level in *A*, *B* and *C*-boilings, going from *A*-boilings to *C*-boilings from 6.4 to 5.7, the calculated sucrose loss as a result of inversion is of a magnitude of 0.8 to 1.0% of pol in syrup. In refineries with refined sugar crystallization of liquors to the last refinery run off, used for reprocessing, it was found that the minimum loss was of a magnitude of 0.2% of the sucrose in first liquor. In some refineries where the pH control showed an average low pH and lack of uniformity in the pH of the processed liquors, this loss could be as high as 0.8%.

For reduction of losses in the crystallization process the pH control is mostly important. Usually it is possible, by introducing a careful system of operation, to reduce these losses to the minimum averages as indicated above, without the introduction of complicated control systems or new systems of pH adjustment.

It is, however, of great importance to the sugar industry over the whole world that a detailed investigation be made on the inversion rate of sucrose in concentrated and low purity solutions, and that the relationship between rate of inversion, different systems of pH determinations, temperature and purity (including the effect of certain types of nonsugars) be determined.

A number of observations in older literature on the effect of neutral salts and amino acids on the rate of inversion as, for instance, found in publications by PRINSEN GEERLIGS and NOEL DEERR² have no more validity today; since this was published, a better understanding of the meaning of pH has been acquired and we have at our disposal reliable methods for determination of the pH. It is primarily the pH that determines the rate of inversion. The observations reported in these older publications have to be interpreted as the effect of added neutral salts on the resulting pH-values. There is not a neutral salt effect on the rate of inversion; there is a neutral salt effect on the pH of the technical sugar solution.

The discussion on sucrose inversion can be reduced to pH, temperature, purity and time. There is an effect of nonsugars on the pH-change of sucrose solutions in concentrating and in diluting. The pH-change, as affected by the presence of certain types of nonsugars, on concentration and dilution is one of the fundamental investigations for a better understanding of the actual H-ion concentration of crystallizing sugar solutions.

3. Decomposition of Reducing Sugars

The reducing nonsugars, as present in the mixed juice in canesugar mills, consist mainly and practically exclusively of levulose and dextrose. The

ratio of these two components is in mixed juice not exactly 1 : 1 as in pure invert sugar; it is possible that there is an excess of levulose over dextrose, and it is also possible that this ratio is an excess of dextrose over levulose. The ratio dextrose-levulose is determined by physiological conditions existing in the cane at the time of harvesting, maturity and age of the cane.

There are indications that when cane is immaturesly harvested or that the harvested cane field is heterogeneous as to age of the different types of cane stalks (old primary stalks with a large number of young shoots and secondary stalks of different ages, etc.), levulose is in excess over dextrose. When cane is overmature or in juices from cane that has flowered, dextrose is in excess over levulose.

In the juice purification we have a number of transformations of the reducing sugars. These transformations are of a complicated nature. The first result is that the transformation products have still reducing powers on an alkaline copper solution. The change in reducing power manifests itself in a change in the reducing power of this group of nonsugars from mixed juice to clarified juice with a change in the specific left rotation of the reducing sugars.

TABLE 3
CHANGES IN REDUCING SUGARS FROM MIXED JUICE TO SYRUP

	Brix	Pol/20° C	Clerget sucrose	Apparent purity	True purity	Reducing sugars	Red. sugars % pol
Mixed juice	15.8	12.8	13.3	81.0	84.2	1.35	10.6
Clarified juice	16.8	13.8	14.2	82.1	84.5	1.20	8.7
Syrup	65.4	54.1	55.5	82.7	84.9	4.72	8.7

	App. nonsugars (brix — pol)	Reducing sugars	Reducing sugars % nonsugars	Sacch. — pol	Reducing sugars	Specific rotation of reducing sugars
Mixed juice	3.0	1.35	45.0	0.5	1.35	— 36 ° V
Clarified juice	3.0	1.20	40.0	0.4	1.20	— 33 ° V
Syrup	11.3	4.72	41.8	1.4	4.72	— 30 ° V

When it is stated that there is a limited change in reducing power of the reducing sugars from mixed juice to clarified juice, it must be understood that this statement is only valid under normal conditions of processing (uniform liming, no excessive alkalinities, etc.). When there is overliming (pH over 8.2), the reduction in reducing power of the reducing sugars can be as high as 30%.

It is customary in many factories to have a determination of the reducing sugars in mixed juice, clarified juice and syrup, and to report the ratio between the reducing power of the sugar juices, expressed as invert sugar units, determined with Fehling copper solution, in relation to the polarization of the same material. This quotient is usually called the glucose quotient (invert sugar quotient or reducing sugars-pol quotient). The correct expression is reducing power-pol quotient; the value that is actually determined is the reducing power of a technical sugar solution reacting with an alkaline copper solution. The reducing substances are neither pure glucose nor pure invert sugar. It is probably within certain limits still reducing sugars. It is rational to call these non-sucrose components reducing substances or reducing nonsugars.

Normal changes in this reducing power are, for instance, as given in Table 3.

Abnormal changes observed in factories where there existed the impression with the factory staff that the liming and clarification were conducted in a proper way (but where the check on the uniformity of the pH of the limed juice did show considerable actual fluctuations, although the average pH of the limed juice was 7.6 and of the clarified juice 7.1) gave figures as represented in Table 4.

When this system of 'glucose' control is continued from syrup to 'pure' *A*-strikes made with syrup, it is found that there is a continued loss in reducing power of the nonsugars. The reduction of a copper solution by a

TABLE 4

CHANGES IN REDUCING SUGARS FROM MIXED JUICE TO SYRUP
(IRREGULAR LIMING, VARIABLE RECORDED pH OF CLARIFIED JUICE 6.7-7.4)

	Brix	Pol	Clerget sucrose	Apparent purity	True purity	Average pH	Red. sugars	Red. sugars % pol	Red. sugars % non- sugars
Mixed juice	17.2	14.3	14.7	83.1	85.5	—	1.12	7.8	38.6
Clarified juice	18.1	15.4	15.7	84.9	86.7	7.1	0.97	6.3	35.9
Syrup	64.4	54.4	55.7	84.4	86.5	6.7	3.71	6.8	28.5

certain amount of nonsugars from mixed juice via clarified juice, syrup to *A*-massecuite has the tendency to decrease. When the same nonsugar reducing power is determined for a *B*-massecuite, the tendency exists for a slight increase, indicating a small inversion of sucrose and the formation of reducing sugars. With *C*-massecuite there is an increase in reducing

power of the nonsugars till a certain stage of the boiling process. At the end of the boiling process and during the processing of *C*-massecuite in crystallizers there is again a decrease in the reducing power per 100 nonsugars.

We are confronted with a number of extremely complicated reactions:

(a) Reducing sugars are present as dextrose and levulose in mixed cane juice.

(b) Transformation of these hexoses during clarification.

(c) Transformation and changes in specific rotation of the mixture of reducing substances during heating and concentrating in evaporators.

This change in the rotation is usually called mutarotation or the mutarotation reactions, meaning the change in rotation.

(d) A slight inversion of sucrose in the pans with formation of reducing sugars.

(e) Reducing sugars transformed specifically at higher concentrations in pans and during the crystallization process are reacting with different types of nonsugars, specifically the amino acids, as a first step in the browning or MAILLARD reaction.

Reaction (e) becomes important in the low grade boilings in the final concentration in the pans with a low water content and relatively higher temperature of some parts of the pan content. This reaction has the tendency to continue in the crystallizers. It does not even stop when the final molasses is eliminated from the massecuite; it continues in the stored molasses in the storage tanks. This last reaction is usually combined with the formation of CO_2 , which is eliminated from the massecuite or becomes visual in stored molasses as foam or froth.

This decomposition of reducing sugars under factory conditions, once it has started in the clarification has the tendency to continue in evaporators and in the pans.

Studies made on processing cane juices at extreme alkalinities as applied in the carbonation process have amply demonstrated that at higher alkalinities, the reducing sugars are attacked and transformed to a greater extent than, for instance, under ideal conditions of a simple or double liming process, specifically if there has not been the most accurate control on the temperature during the carbonation process.

A specific reaction taking place in the concentration of juices is a change in the specific optical activity of the reducing nonsugars. Practically all canesugar factories, when a proper technical control has been introduced, are familiar with the rise in purity in simply concentrating juices in the evaporators from clarified juice to syrup.

This increase in purity can sometimes be extremely high. The difference in purity between clarified juice and syrup can be 1 degree or more. This increase in purity cannot be explained by the removal of volatile nonsugars. The amount of volatile nonsugars eliminated in concentration in the form of CO_2 , ammonia and glyoxal (perhaps acetaldehyde and in a few cases traces of methyl alcohol) does not amount to more than 0.03% of the brix.

Also the amount of inorganic nonsugars removed from the juices in the form of incrustation in the evaporator equipment is extremely small expressed as the percentage of the total amount of brix processed, and under no condition can be more than 0.1%.

The rest in the rise in purity is the result of a change in the optical

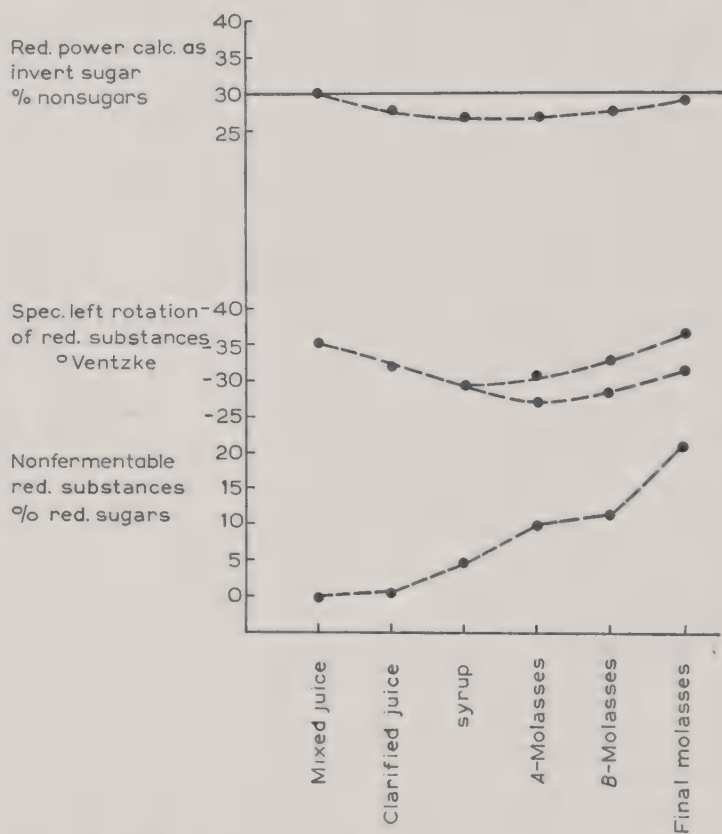


Fig. 5/1. Decrease of specific optical rotation and decrease in reducing power of the reducing nonsugars.

rotation of the reducing nonsugars. The reducing nonsugars show a decrease in the left rotation during concentration. This change is greater when the temperature in the evaporators is higher and the time of processing longer. We have found that with the installation of pre-evaporators, this increase in purity from clarified juice to syrup showed a tendency to increase

with the introduction of higher temperatures in the pre-evaporators or Pauly pans.

Furthermore, it has been found in experiments with evaporators operating under pressure, where juices are concentrated from 15 to 17 brix to a brix of 40 to 45 at temperatures above 100° C, that there is a more pronounced tendency of increase in purity and a corresponding decrease in the specific reducing power of the nonsugars compared to a concentration using traditional conditions under vacuum.

Two factors are interrelated:

- (1) a loss in the specific left rotation of the reducing substances;
- (2) a decrease in the reducing power of the nonsugars as a result of chemical transformations.

The first gives an apparent increase in the purity of the juice and both reactions cause a decrease of the glucose quotient when the control system is based on pol determinations.

A careful check on these phenomena with direct sucrose determinations has proven that both phenomena: decrease of specific optical rotation and decrease in reducing power of the reducing nonsugars, are real. It has been found that when these transformations are studied through the final boilings, both continue normally till the *A*-molasses. In a schematic way these transformations of the reducing sugars are given in Fig. 5/1.

TABLE 5

AMOUNTS OF NONFERMENTABLE REDUCING SUGARS IN FACTORY PRODUCTS. AMOUNTS OF SUBSTANCES USED FOR ANALYSIS: 12 g FINAL MOLASSES, 20 g *B*-MOLASSES, 25 g *A*-MOLASSES, EACH WITH 5 g DRIED FLEISCHMANN'S YEAST; 50 g SYRUP

	Syrup	<i>A</i> - molasses	<i>B</i> - molasses	Final molasses
Brix	62.2	67.3	66.5	91.6
Pol	53.6	34.2	30.4	27.1
Purity	86.1	50.8	45.7	29.5
pH	6.5	—	—	—
Reducing sugars	3.0	12.6	12.8	21.0
Nonfermentable sugars	0.10	1.50	1.66	4.15
NFS/RS	3.3	11.9	13.0	19.8

A most interesting subject is the transformation of the reducing nonsugars in nonfermentable reducing nonsugars during the crystallization process. This reaction is described in a number of monographs, for instance, by SATTLER³ who has studied the presence of nonfermentable reducing substances in great detail in cooperation with ZERBAN.

We have had the opportunity to study the formation of these nonfermentable reducing substances during the crystallization process in raw sugar mills. To get an impression of the presence and formation of the amounts of nonfermentable reducing substances in syrup, *A*-molasses, *B*-molasses and the corresponding final molasses, a large number of analyses of corresponding samples have been made, as given as example in Table 5.

To study the changes in the nonfermentable reducing substances in crystallizers, we have followed the change in composition of the reducing substances in a crystallizer from the moment it has been dropped from the pan till the final molasses leaving the centrifugals. This study resulted in the data as given in Table 6.

From these data had to be concluded that there was no increase in the nonfermentable reducing substances as a result of the reheating in the crystallizers. There was an increase during the cooling period. This usually happens in the first stage of the cooling when the massecuite has a temperature over 60° C.

The reaction between amino acids and reducing sugars is undoubtedly of great practical significance to the sugar industry. The number of studies in the literature on this subject, usually described as the browning or MAILLARD reactions, is extremely great⁴. The study of this combination and the velocity of reacting is usually based on the formation and determi-

TABLE 6
INCREASE OF NONFERMENTABLE SUGAR IN CRYSTALLIZERS

	Molasses cyclone sample taken at time of entering massecuite in crystallizers; temp. 171° F (77° C)	Molasses cyclone sample taken after cooling; temp. massecuite 100° F (38° C)	Molasses from centrifugals after reheating to 120° F (49° C)
Brix	—	—	91.5
Pol	—	—	—
Purity	36.3	31.8	29.6
Crystal content massecuite	35.2	—	41.0
Reducing sugars	19.3	21.1	21.8
Nonfermentable sugar	3.31	4.35	4.51
NFS/RS	17.1	20.6	20.7

nation of 5 hydroxy-methyl-furfural. It is believed that the quantity of 5 hydroxy-methyl-furfural correlates with the intensity of the MAILLARD reaction. The products of the MAILLARD reaction are accumulated in molasses of low purity and lowest water content. They are not very stable and may be converted to other products upon dilution.

It is certain that the sugar-amino acid reaction products can be dehydrated in two different ways; in neutral and at lower densities or in weak acid solutions furfurals are formed, but in a medium of low moisture content, so called reductones (a term introduced for the indophenol reducing substances) can be formed.

The sugar-amino condensation is the first step in the reducing sugars transformation, without 'apparent' sugar-amino condensation in the final product. After condensation and rearrangement of this condensation compound, the sugar 'group' is dehydrated. Polymerisable and unsaturated compounds are formed in which the amino 'group' is labile and can be split off partly from the dehydrated sugar residue which is characterized by its brown color. This group of products is called melanoidins; it is a mixture of different brown nitrogenous polymers and copolymers.

The combination of the destruction and transformation of reducing nonsugars and the inversion of sucrose takes place simultaneously during the crystallization process.

The number of quantitative studies on the reaction velocities with technical sugar products as met in cane and beetsugar factories and refineries is limited. One of the papers giving a description of this kind of reactions in a quantitative way has been presented recently by THOMPSON, GARDINER and DE WHALLEY⁵.

Sucrose Losses in Pan Boiling

Some studies have been made on sucrose losses in crystallizer work, but the exact determination of sucrose losses during the crystallization in pans requires, firstly, a special laboratory technique and, secondly, a special type of analysis to be absolutely certain that the observed changes in the composition of massecuites can be related to an actual destruction of sucrose.

THOMPSON, GARDINER and DE WHALLEY have made an investigation where all entrainment losses were completely eliminated and where the material to be crystallized could be determined quantitatively for complete analysis before and after crystallization. The total invert sugar was determined by invertase inversion using the LANE and EYNON titration method. Solids in boilings were analyzed with the refractometer, corrected for invert and ash content. The results obtained in this experiment are given in Table 7. The loss of total sugars in affination syrup boilings and first and second crop sugars was 0.17, 0.26 and 1.01 %, respectively. The amount of reducing sugars gained was 1.24, 0.84 and 0.48, respectively. The amount of sucrose lost was 1.41, 1.10 and 1.49, respectively.

The result is that with a decrease in purity of the massecuite, a higher

proportion of the reducing sugars is broken down. A reasonable assumption is that the destruction of levulose would be greater than the decomposition of dextrose; but the determination of these two components is not in agreement with this assumption. A part of the reducing sugars produced and lost during the boiling process is transformed into nonsugars without or with a reduced reducing power.

The total solids balances show that these losses are considerably lower than the sugar losses. For the first crop syrup boiling the total loss was 0.06% and for the second crop syrup boiling 0.25%. The solids losses are approximately $\frac{1}{4}$ of the total sugars lost.

The amount of sucrose lost during the boiling of affination syrup and first and second crop sugars is 1.1 to 1.5% and does not differ much for the three materials investigated.

TABLE 7

	Affination syrup massecuite; boiling time 6 h 22'	First crop sugar massecuite; boiling time 6 h 30'	Second crop sugar massecuite; boiling time 10 h
Sucrose	55.1	44.8	29.9
Reducing sugars as invert sugar	4.35	9.55	16.4
Total solids (refr.)	66.75	63.9	63.5
Ash	2.71	3.92	7.2
Purity	82.5	70.1	47.1
Red. sugars-ash ratio	1.61	2.44	2.28
Sucrose loss % total sugars	— 1.41	— 1.10	— 1.49
Red. sugars gain % total sug.	+ 1.24	+ 0.84	+ 0.48
Loss in total sugars %	— 0.17	— 0.26	— 1.01
Loss of total solids %	—	— 0.06	— 0.25
Dextrose in massec. % brix	2.09	—	6.9
Levulose in massec. % brix	2.27	—	7.0
Total dextr. and levulose % brix	4.36	—	13.9
Red. sugars acc. to LANE and EYNON	4.97	—	16.6
Other red. substances	0.61	—	2.7
Other red. subst. than dextr. and lev.	12.3	—	16.3
% total red. sug. acc. to LANE and EYNON	— 0.22	— 0.17	— 0.15
Sucrose loss per hour % total sugars	+ 0.20	+ 0.13	+ 0.05
Red. sug. gain per hour % total sug.	— 0.24	— 0.21	— 0.23
Sucrose loss per hour % sucrose	+ 2.75	+ 0.74	+ 0.08
Red. sugars gain per hour % red. sug.			

The amount of reducing sugars produced and decomposed increases with a decrease of the purity of the massecuite.

Endeavors made in operating sugar mills for quantitative balances of reducing sugars and sucrose to determine the nature of the losses, respectively to calculate the chemical losses and the undetermined losses resulting

from entrainment and other causes in a sugar factory or refinery, have practically never given satisfactory results. This is understandable; we are dealing with a number of transformations.

We must also realize that the analytical methods we are applying do not always result in quantitative figures representing accurately the compound of which we wish to know the exact quantity present. Even the determination of sucrose by double polarization or via the determination of the reducing power after inversion has an unavoidable experimental error in the calculated results. For sucrose we may assume that when the analysis is made with all possible precautions and analyzing the sugar solutions at a standardized constant temperature (which is a condition existing only in a few sugar factory laboratories), the accuracy is as follows:

Pol mixed juice	$\pm 0.1\%$
Pol final molasses	$\pm 0.6\%$
Sucrose mixed juice	$\pm 0.1\%$
Sucrose final molasses	$\pm 0.3\%$
Brix mixed juice	$\pm 0.1\%$
Brix final molasses	$\pm 1\%$

With these accuracies in mind and realizing at the same time the unavoidable errors in the weighing of juice, sugar and molasses, a sucrose balance can never have a greater accuracy than $\pm 0.3\%$ of the calculated sucrose account.

In the balance of the reducing sugars starting with mixed juice it is even totally impossible to make a balance of *reducing sugars* based on the reducing power, by the different changes taking place in the reducing sugars as a result of transformations, combinations and decompositions. When a factory reports that of the total reducing sugars in mixed juice 10 to 15% has been lost in processing, the meaning of such a report may be that the original reducing sugars have been transformed to such an extent that 10 to 15% of the original reducing power has been destroyed in some way or another. It is more correct to use the term reducing substances for the nonsugars reducing an alkaline copper solution. The best expression is the reducing capacity of sugar products expressed in invert sugar equivalents.

By repeated systematic technical control we can get an impression of the nature of the different transformations and possible losses. After a careful analysis of at least 10 periods of operation we are justified in making a definite statement as to the probable changes in losses occurring in the processed sucrose and processed reducing nonsugars.

It is certain that quantitatively speaking, the transformation of reducing sugars into nonfermentable reducing substances occurs specifically in the

last product boilings and especially in the last phase of the processing; temperature and concentration, respectively water content in this last phase of crystallization are the main factors for the formation of this type of reducing substances.

How far this reaction is influenced by the presence of certain types of nonsugars, for example heavy metal cations as iron and copper acting as catalysts, is not known exactly; however, there are indications that iron accelerates the formation of nonfermentable reducing substances. The question of prevention of this reaction, respectively reduction of the reaction velocity by the addition of sulfites, is still unanswered although there are indications that the use of hydrosulfites in low product boilings in the quantities usually recommended (or being a traditional practice) for sugar manufacture does not result in an appreciable reduction of the formed amounts of nonfermentable reducing substances.

4. Reactions of Organic Nonsugars

Our knowledge of the reactions of organic nonsugars, except reducing nonsugars, during the crystallization process is imperfect and deficient. We know that some organic acids become insoluble under the conditions of the crystallization process in the form of calcium and magnesium salts as, for instance, calcium-magnesium aconitate and calcium oxalate.

It is also known that some of the amino acids combine with the reducing sugars, which can be demonstrated via the nitrogen content of a filtered fermented diluted molasses solution where a part of the nitrogen (correlated with the amount of nonfermentable reducing substances) is not able to act as a nutrient for growing yeast but remains as a soluble nitrogen containing organic compound in solution. This reaction can be demonstrated by using the reaction products of pure amino acids and reducing sugars as nutrient for growing yeast. This nitrogen compound cannot be assimilated by *Saccharomyces* or *Torula* yeast; pure amino acids are easily absorbed by growing yeast. The presence of certain types of organic nonsugars, specifically starch and some of the polymolecular carbohydrates especially in the group of pectins (sometimes called gums), can affect the crystallization. It has been found that they are able to syncrystallize with the sucrose and are incorporated in the interior of the solid sugar crystals. This subject will be discussed in a following paragraph.

A certain group of nonsugars belonging to the organic nonsugars becomes insoluble during the concentration process in vacuum pans and accumulates in the mother liquor. They can be isolated by centrifuging the

molasses diluted to 60 to 65 brix. This insoluble material is a complex mixture of precipitated and coagulated nonsugars.

How far we are dealing with real precipitation of nonsugars as a result of the fact that they become supersaturated during concentration, and how far we are dealing with a coagulation as a result of a prolonged heating in the pans, the high density of the solutions, and the instability of these nonsugars, being more or less a metastable colloidal dispersion in the diluted materials, clarified juice and syrup, is not known because we are not able to distinguish and have not tried to determine the nature of these different groups of impurities.

However, when concentrating and desugaring material in the crystallization process, some of the nonsugars precipitate. Among this group are also organic nonsugars. This precipitation increases with the desugaring, and the amount of precipitated nonsugars % nonsugars increases from *A*-boilings to *C*-molasses as demonstrated by the data given in Table 8.

There are a number of reactions of great practical significance of which we observe only the end-result in the form of color formation without being familiar with the mechanism of the reactions actually taking place.

In the older literature it was common to call this color formation caramel formation or caramelization. But this general term is not sufficient to describe the nature of the color formation in the boiling process. Cara-

TABLE 8

INSOLUBLE AND SUSPENDED NONSUGARS IN SYRUP, *A*-, *B*- AND FINAL MOLASSES IN RAW CANESUGAR MILL RECOVERABLE BY CENTRIFUGAL SEPARATION (SEE VOL. I, P. 319)

	In mg per kg of nonsugars			
	Syrup conc. to 70 brix	<i>A</i> - molasses	<i>B</i> - molasses	Final molasses
Total suspended solids	2000	3000	4000	5000
Inorganic	1500	2000	2700	3200
Lipids	110	90	80	60
Pentosans	45	60	90	110
Proteins (N × 6.25)	125	180	180	250
Not determined organic substances	200	500	800	1400

melization is the decomposition of sugar or sugars at higher temperatures with a dehydration and a polymerization of the dehydrated molecules and the formation of complex molecules and substances present in diluted sugar solutions in a colloidal form with a higher carbon content and a lower H₂O content. These are end-product substances which can be described

as humous compounds or humic acid and can be coagulated with polyvalent cations as calciumhumate or calciumcaramelate, or combined with aluminum ion but which are in all probability no chemical compounds but colloidal organic material having absorbed a certain amount of calcium or aluminum ion.

TABLE 9

COLOR CONCENTRATION DETERMINED IN A BRIX SOLUTION FILTERED OVER PURIFIED ACID WASHED KIESELGUHR, pH = 7.0, WAVE LENGTH 500 m μ
(RAW SUGAR MILL — COIL PANS)

	App. purity	Color concentration per °brix	Color % nonsugars
Syrup	84.0	0.120	0.75
A-boiling	83.2	0.141	0.84
B-boiling	73.0	0.284	1.05
C-boiling	59.4	0.487	1.20
C-sugar	88.2	0.147	1.25
Final molasses	31.5	0.795	1.16

The practical significance of this reaction is that we try to reduce color formation to a minimum by the ways and means we have at our disposal in sugar manufacturing. Overheating must be avoided. A high temperature increases the formation of colored decomposition products. The presence of iron even in small amounts is affecting the color formation in sugar products in process. The addition of sulfites is able to prevent the formation of coloring substances probably indirectly by reducing the ferric iron to ferrous iron. It is, however, inevitable that the amount of color per 100

TABLE 10

PERCENTAGE INCREASE IN COLOR CONCENTRATION PER 100 NONSUGARS IN THE BOILING PROCESS IN CANESUGAR FACTORIES

	Raw sugar factories	Carbonation factories	Sulfitation factories
From syrup to A-boilings	10-15	5-10	5-10
From syrup to B-boilings	20-30	15-20	15-25
From syrup to C-boilings	30-50	20-30	25-45

nonsugars increases with the time of processing; the color formation per 100 nonsugars per unit of time increases with a decrease in the purity of the sugar products.

In Table 9 we give an example of the color concentration of different types of sugar house products in canesugar factories.

The intensity of this color formation in the manufacturing process, regardless of its simplicity, has only been studied in a few countries and in a few exceptional cases. Most of these studies, as far as the canesugar industry is concerned, have been done in Java comparing different types of boiling schemes and purification methods as to the effect of system of purification and system of boiling on color and color formation. In Table 10 we give a summary of these color formation studies collected in the Java sugar industry between 1928 and 1940.

A practical important point is that in the crystallization process, where it is a necessity that the pans after discharging the massecuite are cleaned thoroughly to remove the remaining massecuite on heating surfaces and walls, the color intensity of these steamings per 100 nonsugars has been found to be considerably higher than the color concentration of the main bulk of the massecuite per 100 brix as well as per 100 nonsugars. Even with what was considered to be the best type of pan it was found that there was always a certain amount of caking of the massecuite on the heating surfaces which was not removed by the circulating massecuite but remained in contact as a kind of crust or caramelized massecuite as

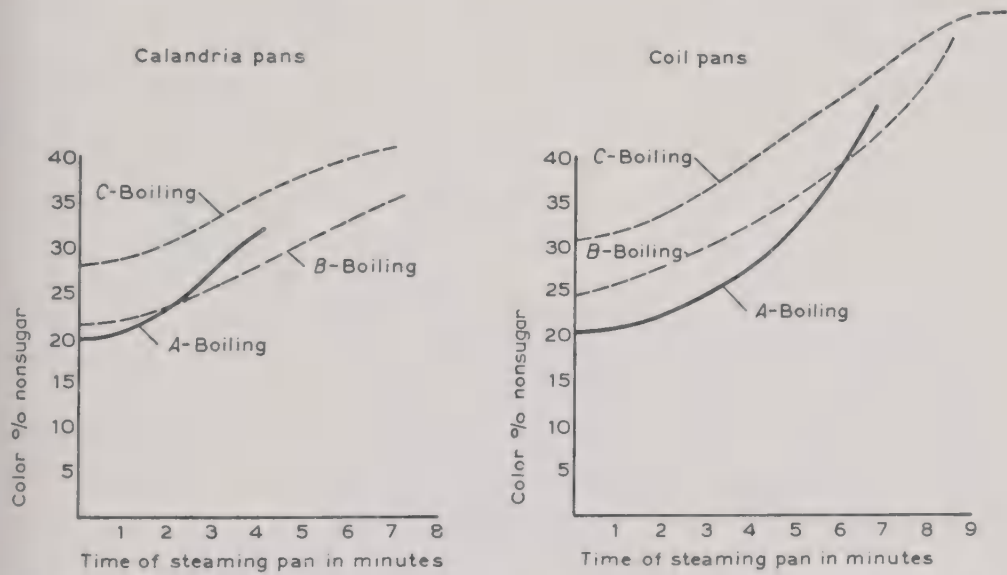


Fig. 5/2. Color concentration in steamings of pans in raw canesugar factories.

found in cooking porridge in a kitchen pan. These localized crusts were characterized by a high color concentration.

It was also notable that to a certain extent the color concentration of the steamings of a pan could be used as an indication for the circulating and self-cleaning efficiency of the pans. If a pan had a well-constructed calandria

or a system of heating coils with a minimum of resistance against the circulation and if the boiling process was conducted without any stagnation, it was found that the color concentration of the steamings of such pans had a much lighter color than that of so called sluggish pans or of pans where the normal boilings had been interrupted with a temporary stagnation in the circulation.

In Fig. 5/2 we give some data on the color concentration of steamings or washings of sugar pans in comparison to the color of the bulk of the massecuite.

5. Phenomena Related with the Different Types of Inorganic Nonsugars

Crystallization of sucrose is the process of bringing the concentration of technical sugar solutions to such a point that the sugar becomes saturated and is precipitated from the solution. Simultaneously with this increase in concentration of sucrose, the impurities are brought to a higher concentration. Some of these nonsugars become, as we know by practical experience, supersaturated and precipitate with the sucrose.

The saturation solubility of some of these nonsugars is reached more easily than for others. For instance, in technical sugar solutions, except in highly concentrated final molasses, the precipitation of sodium and potassium chloride and sulfate practically does not occur. An exception has to be made for the precipitation of potassium chloride. It was found in Hawaii in 1952⁶ that potassium chloride was able to crystallize in low grade boilings (occurring as early as in *C*-footings in seed pans) and in the final stage in crystallizers. These potassium chloride crystals are easily mistaken for false grain; they are minute cubic crystals. The size of these crystals is such that they do not interfere with the purging process in the centrifugals. The amount of potassium chloride crystals found in low product boilings was affected by cane variety and type of irrigation.

The final molasses where this precipitation of KCl occurred had an ash content of 15%, with a reducing sugar content of 10%. This is an exceptional ratio of reducing sugars and ash. The ash contained approximately 45% K_2O , 8% Na_2O , 11% CaO and MgO , 11–12% SO_3 and 21–22% Cl .

A normal inorganic constituent precipitating in concentrating technical sugar products in canesugar factories is calcium-magnesium aconitate. This is one of the normal impurities present in precipitated form as fine crystals in low grade boilings.

But the most common impurities precipitated in the crystallization

process are different types of calcium salts: calcium sulfate, calcium sulfite in sulfitation white sugar factories, calcium fosfate, and different types of calcium organates.

The precipitation of calcium salts is a normal phenomenon in all technical crystallizations in cane and beetsugar factories. The amount of calcium and sulfate present in syrup in normally operating mills reaches, practically under all conditions when technical sugar solutions are concentrated to the point that the sugar becomes saturated, the maximum solubility of calcium sulfate. In technical sugar solutions, the calcium sulfate precipitates as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This precipitation can also be observed as a fine cloudiness in the run offs of refined sugar strikes and in the high purity boilings in raw sugar mills. It demonstrates itself by an accumulation of calcium salts in the purged sugar, where we find normally a higher percentage of CaO on ash than present in the run offs or molasses.

It is for this reason that the control on the calcium content of juices and liquors has received so much attention from practical sugar technologists because it was recognized a long time ago that the calcium content showed a direct effect on the quality of the manufactured sugar.

In high grade liquors in refineries it is found, when CaO in liquor surpasses 350 parts of CaO per million parts of sucrose with an amount of sulfate of approximately 200 parts per million parts of sucrose, that a part of the CaO is precipitated during the crystallization process and is held back by the sugar layer in the centrifugals as an impurity in the final product.

During the time that refining of sugar was still surrounded by a number of secret practices it was, for instance, customary in some of the European refineries to add a small amount of BaCl_2 to the raw liquors to precipitate sulfate that in concentrating the liquors in the pans, the solubility product $\text{CaO} \times \text{SO}_4$ would not be surpassed. Another practice was the use of small amounts of oxalate before the bonechar filters to precipitate a part of the lime salts.

That these practices were surrounded with secrecy is understandable because in many countries the use of oxalates and barium salts in food processing was not permitted. But these old practices showed that there was a realization of the harm that could be done by the presence of calcium and sulfate in manufacturing a high grade refined sugar.

The great advantage of the use of bonechar over other refining methods is that bonechar removes calcium salts to a considerable and sulfate to a limited extent. The use of fosfatation in combination with small amounts of vegetable carbon tries to achieve the same effect, although the claimed effect of fosfatation in lime removal in high grade liquors should not be

exaggerated. The fosfatation removes more magnesium salts, which are in themselves harmless as to the quality of the refined sugar because magnesium salts in high grade liquors are soluble and only become insoluble in low grade products as calcium-magnesium aconitate and as calcium-magnesium fosfates.

(a) *How is the Presence of Inorganic Suspended Solids demonstrated in Commercial Sugars?*

The simplest way to demonstrate the presence of insoluble inorganic nonsugars in the manufactured sugar is by determining the reducing sugars-ash ratio in the commercial sugar and the reducing sugars-ash ratio in the final molasses.

If there is no accumulation of insoluble ash in the commercial sugar, these two ratio figures are identical; but if we find RS-ash ratio commercial sugar = 1.4 and RS-ash ratio final molasses = 2.0, we have to conclude that there is a relative accumulation of inorganic nonsugars present as insoluble nonsugars in the commercial sugar.

Finding for the analysis of sugar and final molasses the following data:

Commercial sugar:	reducing sugars	0.62
	sulfated ash uncorr.	0.44
	RS-ash ratio	1.4
Final molasses:	reducing sugars	23.0
	sulfated ash uncorr.	11.5
	RS-ash ratio	2.0

the amount of soluble ash in the commercial sugar is:

$$\frac{\text{reducing sugars in commercial sugar}}{\text{RS-ash ratio in final molasses}} = \frac{0.62}{2.0} = 0.31\%$$

or the amount of insoluble ash in the sugar is:

$$\text{ash in commercial sugar} - \frac{\text{reducing sugars in sugar}}{\text{RS-ash ratio in final mol.}} = 0.44 - 0.33 = 0.11\%.$$

Why are we interested in insoluble ash in the manufactured sugar? The insoluble ash in manufactured raw sugar affects the filtrability. The higher the insoluble ash, the lower the filtrability. In the second place, the insoluble ash is always high in CaO and has the tendency to redissolve partly in raw sugar melts and increase the CaO content of the melts. The accumulation of precipitated nonsugars is mostly pronounced in the final products of raw sugar factories.

(b) *Different Methods of Determining the Amount of Insoluble Nonsugars in Molasses and C-sugars*

As most of the insoluble nonsugars in *C*-sugar are inorganic, it is possible by using the RS-ash ratio as a yardstick to calculate the accumulation of insoluble ash in *C*-sugars. Under accumulation of insoluble ash must be understood in this case the accumulation of ash in an insoluble state that is filtered off by the sugar layer in the centrifugals. It is not identical with what is understood by insoluble ash in a physical chemical sense. Also, the final molasses contains a certain amount of insoluble ash but in such a fine dispersion that it is not held back by the pores and capillaries in the sugar layer in centrifugals.

The other method is by separating the insoluble matter in a centrifugal separator, for instance, a De Laval separator.

The difference with the first method is that for the separation of these suspended nonsugars it is necessary to dilute the molasses and to dissolve the *C*-sugar. In practical experiments molasses is diluted: 1.5 kg of molasses with 1 kg of water; the *C*-sugar is dissolved by using 2 kg of *C*-sugar with 1.5 kg of water. The temperature of this separation in a De Laval is 55° to 70° C. The centrifugation rate must be adjusted for a De Laval separator 300 in such a way that 2 l of liquor are treated in approximately 15 minutes. The difference is that in this case the liquor is diluted and that a part of the insoluble impurities may be redispersed or even redissolved. On the other

TABLE 11

ASH IN MOLASSES AND *C*-SUGAR

	Ash % molasses	Ash % molasses in <i>C</i> -sugar	Difference = insoluble ash per 100 g molasses in <i>C</i> -sugar	Molasses % crystal	Insoluble ash % crystal
Factory	16.5	23.0	6.5	33.7	2.2
Laboratory	15.6	34.7	19.1	19.9	3.9
Factory	17.5	19.8	2.3	30.7	0.7
Laboratory	17.3	28.3	11.0	26.9	3.0

hand, an advantage is that the nonsugars can be accumulated in this way in a concentrated, fairly pure form and can be analyzed in detail to determine the main components.

Studies made in this field of the composition have shown that most of these suspended nonsugars are inorganic and consist of calcium-magne-

sium fosfate, calcium-magnesium silicate, calcium organates, sometimes calcium sulfate, with a certain amount of lipids (fatty acids, cane wax alcohols, true cane wax) and sesquioxides partly present as a combination of sesquioxides and silicic acid of the general formula $(R_2O_3)_2(SiO_2)_n$.

In an investigation where the final *C*-massecuite was centrifuged by the

TABLE 12
INSOLUBLE ASH IN MOLASSES AND *C*-SUGAR, DETERMINED DIRECTLY
BY CENTRIFUGATION

Insoluble ash in 100 g final molasses	% insoluble ash in <i>C</i> -sugar	Crystal content <i>C</i> -sugar	Insoluble ash per 100 g molasses in <i>C</i> -sugar	Insoluble ash per 100 g crystal
0.52	1.00	76.7	4.2	1.3
0.77	0.29	83.7	1.8	0.35

factory centrifugals and the *C*-massecuite in a laboratory centrifugal, the results were as given in Table 11.

How far these differences are related to differences in the way the massecuite in the centrifugal is brought at an accelerated gravity force in the laboratory centrifugal compared to the factory centrifugal, causing a greater compactness to the sugar layer, is difficult to say but it may be that this is one of the causes of the observed differences for the molasses in *C*-sugar.

Using a different technique for the determination of suspended insoluble nonsugars by centrifugation of the diluted molasses and the dissolved *C*-sugar in a De Laval separator, the results were as given in Table 12.

Progress in practical sugar manufacturing has to be made primarily by the development of purification techniques which remove the nonsugars precipitable under the conditions existing in the crystallization technology as applied today.

Application of ion exchangers can have the greatest benefit in raw sugar manufacturing, if we are able to develop economic methods removing CaO and sulfate. The same holds true for the manufacture of refined sugars. For the quality of sugars, the presence of alkali and magnesium salts is, to a certain extent, harmless to manufacture a sugar of a good filtrability and good refining characteristics, meaning that with the simplest system of purification (for instance, by vegetable carbons) a liquor can be produced which can be crystallized without the formation of any nonsugar precipitate. For the yield of recovered sugar, the removal of as much nonsugar constituents as can be economically realized is important. But this is the quantitative aspect of sucrose crystallization.

When referring to the quality of refined sugar and the quality of raw sugar, we should aim to manufacture products that must be almost free of precipitated nonsugars. Another important point in this connection is that we have not only to consider the fact that nonsugars are precipitated in the crystallization process, but also that they are filtered off by the sugar layer in the centrifugals. The porosity of this sugar layer is very important for the retention of the fine precipitates in the mother liquor. When the sugar has a sufficiently large grain size and is uniform, the filter effect will be much less and there will be less accumulation of this finely suspended matter in the sugar. The emphasis that is laid by refiners to receive a raw sugar of uniform grain size is primarily that such a sugar can more easily be washed in the affination centrifugals with a complete removal of the molasses film including the nonsugars present as fine precipitate in this molasses film. Practical experience has demonstrated this over and over again.

At present we have no simple way to eliminate these suspended insoluble impurities, and we must accept the results of our present system of clarification and processing. But one point must be emphasized; one of the worst products in raw canesugar mills as to the amount of suspended matter to be returned to the commercial boilings is *C*-sugar. In *C*-sugar, by its fineness, an extremely high percentage of the precipitable nonsugars is accumulated. A returning back of these impurities to the *A*- and *B*-boilings is a straight contamination of these boilings and introducing an extremely harmful nonsugar to the commercial product. In factories where a direct white sugar is made as, for instance, carbonation and sulfitation white sugar factories, this phenomenon is known for years.

Sugar producing countries specializing in this type of sugar recognized forty years ago that the greatest progress that could be made in improving the quality of the sugars to be made from *A*- and *B*-boilings was the elimination of the molasses film from the *C*-sugars to be returned for reprocessing. This is usually done by double purging. In many cases it is a recommendable practice, when the *C*-sugar is not used as seed nucleus for the final product but has to be remelted, that the *C*-sugar high in insoluble nonsugars is subjected to a special filtration for the elimination of these harmful constituents.

6. Nonsugars Affecting the Crystallization of Sugars

In the crystallization of sucrose we are dealing with a number of phenomena where a certain influence of the nonsugars exists on the nucleation, the velocity of growth of sucrose crystals, the inclusion of impurities in the

growing crystal, and impurities affecting the shape or crystal habitus of the sucrose crystal.

In the nucleation of technical sugar solutions we know as a well established fact that the more impurities are present in the sucrose solution, the greater can be the supersaturation before we have a spontaneous formation of nuclei. At the temperature where the crystallization in vacuum pans is conducted, being normally 70–75° C, it is possible to concentrate canesugar products with a purity lower than 75 to a supersaturation of 1.60 and higher without any spontaneous formation of sucrose nuclei. When the purity is higher, this supersaturation value for nucleation is reduced considerably. For very pure high grade liquors, the nucleation can start at supersaturation values of 1.10.

This is nothing else than a description of observed facts. A theoretical interpretation is not simple. If such explanations have been given, they have neither a solid physical or chemical foundation nor do they have great practical value for guiding the nucleation process.

The crystallization technique as to the nucleation has been simplified in recent years tremendously by the full seeding technique, which has eliminated, in many countries and anyhow in the majority of modern sugar factories, the old system of nucleation by waiting or by using special operational techniques as concentrating at a reduced vacuum at higher temperatures and increasing more or less suddenly the vacuum with a corresponding temperature drop. This in itself was a very erratic system and could never be qualified as a rational operational technique.

The first rule to be stated is that the amount of impurities in technical sugar solutions increases the stable zone of supersaturation in which under practical conditions the formation of new sucrose nuclei does not occur. When a careful study is made of the supersaturation values to which a technical sugar solution can be concentrated without spontaneous nucleation, considerable fluctuations from factory to factory can be observed.

It is not possible at present to give a simple explanation of the fundamental cause of these observed differences. We found that it was possible at some cane factories to concentrate *A*-molasses at a purity of 72 to 75 without nucleation to a supersaturation of 1.80. With this supersaturation the pan could be easily seeded with fondant sugar without the formation of extra nuclei. But at other factories, it was found that the maximum supersaturation at the same purity level could not surpass the 1.50, or the application of the full seeding system resulted at the same time in a formation of a large number of extra nuclei and the full seeding system was transformed into a shock seeding system.

The second process where the impurities affect the crystallization is the velocity of crystal growth in a supersaturated solution. This subject is discussed in details in the chapters written by VANHOOK.

In this respect the variations at the same purity level between different factories are much more considerable. There are undoubtedly a number of impurities retarding the velocity of crystallization. It is certain that in pure sugar solutions the growth of a crystal surface to form the complete lattice plan is an extremely rapid process compared to the formation of the nucleus or seed. We also know that once the habitus of a sucrose crystal has been formed, it remains more or less the same when the growth of the crystal continues. We also know that the most perfect crystals are formed when there is a slow rate of growth as, for instance, in the manufacture of large candy crystals, or in boiling at low supersaturations. Once the shape of a crystal has been determined as a twin crystal or a needle-like crystal or flat sucrose crystals in the very first beginning of the crystallization to a grain size of 0.05 mm linear, it can be observed that normally this crystal shape continues to the full grown final crystal.

Undoubtedly, certain impurities determine the characteristics of the final sucrose crystal. We know that when the nucleation in canesugar factories is done at rather high supersaturations with a high percentage of reducing sugars, there is a tendency to the formation of twin crystals. There is in the beginning of the crystallization a kind of competition on the growing crystal surface between sucrose in supersaturation and impurities. The impurities can be a fundamental factor in determining the habitus of the sucrose crystal.

We also know that there are certain types of impurities affecting the rate of crystallization to a great extent. This is well known from studies on crystal growth done with other substances than sucrose. We know also that certain impurities have a much greater effect at lower temperatures on the rate of crystallization, for instance, in crystallizers than in vacuum pans. It seems that the effect of certain types of impurities on the rate of crystallization decreases with the temperature of crystallization.

The sugar industry is at present not able to analyze in a simple standardized way the crystallization characteristics of the normal materials that have to be crystallized in sugar factories and refineries. This makes it nearly impossible to discuss the specific effect of certain types of impurities. What we are reading in the professional literature on sugar technology is more or less generalized without specific meaning. Even when the practical technologist has observed certain phenomena, it is difficult to translate these observations by an objective standard into quantitative values for the efficiency of the crystallization technique.

It is certain that some types of nonsugars affect the growth velocity of sucrose crystals. It is also a recognized fact that each face of the crystal has its own growth velocity. It is found that the different nonsugars can affect the growth of certain faces of the crystal to such an extent that they do not grow at all and that the result of the crystallization is a simplified form of the ideal sucrose crystal.

The nature of the nonsugars having these specific effects is known as a general phenomenon. In synthetic solutions to which a large amount of caramel has been added, the caramel is absorbed at certain faces of the sucrose crystal, syncrystallizes with the sucrose and the caramel can be observed as a colored impurity in the crystal deposited in layers parallel to certain crystal faces.

Another point we know for certain is that it is possible that high molecular impurities, as for instance starch, are also absorbed by growing sucrose crystals, and that it is extremely difficult to make pure sucrose from solutions containing starch as impurity simply by recrystallization.

This phenomenon of the inclusion of impurities has occasionally been called syncrystallization. The nature of this syncrystallization is not simple to understand. For instance, with iron as impurity, it is possible to think in terms of mixed crystals where iron saccharate or ferrate, respectively potassium saccharate is taken up in the crystal lattice as being to a certain extent similar and having affinity for the growing crystal face. But it is also possible that we are dealing with simple adhesion and that the impurity is simply overgrown by the following layers of sucrose.

There are indications that something like this is actually taking place, as is suggested by the extremely fascinating illustrations in the paper by POWERS.

We are confronted with the fundamentals of crystallization if we wish to understand how the impurities are included in growing sucrose crystals. Is the growth of a crystal the incorporation of molecules in supersaturation in a certain crystal lattice or is it possible that we are dealing with larger units more or less deposited as bricks in a wall, and that the dimensions of the elementary units forming the crystal are much bigger than molecular dimensions?

There have been theories on the crystallization such as the formation of submicrons in supersaturated solutions being a group of molecules that is deposited as a conglomerate unit on the surface of a growing crystal, but scientists working on crystallization are telling us that this theory has not a very solid foundation and that the real crystal growth from solutions is taking place in a different way.

The term 'mixed crystals', well known from the field of pure chemistry,

is perhaps only an exception in the phenomena related to the inclusion of impurities in sucrose. This is, for instance, the case with iron as impurity which is extremely difficult to eliminate from syncrystallization. But for a substance as starch we are undoubtedly dealing with quite a different phenomenon.

What we must not consider in this is the inclusion of mother liquor in pockets, cavities, grooves, pores and corners, which occurs when we have the formation of crystal conglomerates. In this case we must not talk about syncrystallization but simply about mechanical inclusion of mother liquor.

Syncrystallization is specifically the inclusion of impurities in sucrose crystals of a normal and ideal habitus as single units. It is quite certain that we are dealing here with an extremely complex process. The purification technique must find primarily ways and means to eliminate impurities which are able to syncrystallize with sucrose. This is for the future one of the greatest problems in the field of original research investigations to make real improvement in the technology of crystallization.

The following facts are observed in the crystallization of sucrose:

(1) The impurities included in sucrose crystals made from technical sugar solutions in cane and beetsugar factories and in refineries show a composition differing from the nonsugar composition of the mother liquor. In the crystallization process of sucrose there is a specificity in the inclusion of certain types of nonsugars in the interior of the crystals.

(2) The impurities included in sucrose crystals are occasionally of a nature that we have to assume that they are present in real solution in the mother liquor during the crystallization process and that these impurities have been absorbed by the crystal faces and are distributed more or less homogeneously in the solid crystal comparable to the formation of mixed crystals. This is found, for instance, for iron and potassium as impurities. These impurities must be sufficiently related to be isomorphic with the parent or host lattice, being the lattice of the sucrose crystal. Other impurities are high molecular substances, as for instance starch, which is found in the interior of solid sucrose crystals. The way this kind of impurities has syncrystallized with sucrose is not quite clear. It is possible that there is an adhesion of the starch molecules at the growing surface and that they are overgrown by the following sucrose layers comparable to an insect sticking to a wet paint coating and covered by a second coating.

(3) Certain colored impurities are absorbed more strongly by specific faces of the growing sucrose crystals. The effect of these impurities with a specific absorption for certain areas of the crystal surface can be so strong that the velocity of crystallization of these faces is retarded to such an extent

that the final habitus of the resulting sucrose crystal is a simplified form, missing some of the crystal faces.

(4) The syncrystallization of impurities must be distinguished from the occlusion of mother liquor in the imperfections of sucrose crystals, forming pockets, grooves and corners, specifically in complex crystals which are overgrown during the process of crystallization by crystallized sucrose and are nothing else than the occlusion of pure mother liquor.

(5) The analytical methods available today for separating the ways of occurrence of different types of nonsugars in crystallized sugar are still imperfect. The simplest way for studying this phenomenon of syncrystallization of sucrose and impurities is the washing of well developed sugar crystals with a saturated solution of pure sugar to remove completely the surrounding film of mother liquor and to analyze the remaining sucrose crystals after dissolving on impurities.

A difficulty in this technique is the complete removal of precipitated nonsugars adhering to the surface of the sucrose crystals by a washing. By this technique it has been demonstrated that, for instance, calcium as impurity in refined sugars is practically exclusively present as a precipitated impurity not included in the interior of the solid sucrose crystals. But iron, on the contrary, as impurity is included in the sucrose crystals and has syncrystallized with the sucrose.

This inclusion of nonsugars is not exclusively determined by the nature of the impurities but also the conditions of crystallization have an effect on the quantitative aspects of the inclusion.

It has been found in special experiments that in the crystallization of refined sugar, the temperature of crystallization has no effect on the amount of colored nonsugars absorbed by the crystallized sucrose. Boiling at 60, 65, 70 and 75° C had no appreciable effect on the color concentration of the solid sugar.

7. Phenomena Related with the Dissolution and Regrowth of Sucrose Crystals

In the technical crystallization of sucrose we are dealing with dissolution of crystals and regrowth. The best known example is the use of *C*-sugar as seed sugar for commercial boilings in raw sugar factories. A *C*-sugar is mixed with syrup, dissolving a part of the sucrose crystals and removing by a washing process the adhering molasses film. It can be observed that the sucrose crystals have been partly dissolved when they are used as a footing for the commercial boilings.

As a result of the transport of the magma through pumps, we will have a mechanical break down of some of the crystals. It is stated occasionally by practical technologists that fractured sucrose crystals heal easily by renewed growth which would occur with greater speed at the broken surfaces. According to careful observations made on this subject, it seems that this

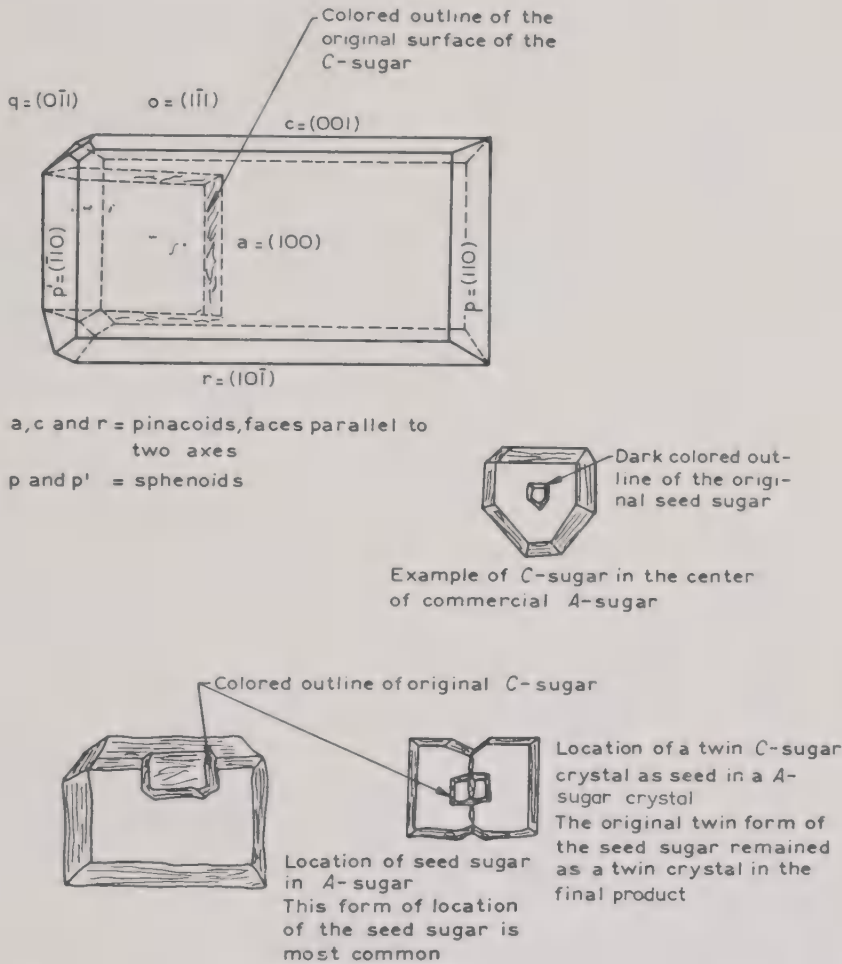


Fig. 5/3. Development of seed crystals (C-sugar) to commercial sugar in canesugar factories.

is a fiction. There is no indication that a broken or partly dissolved crystal surface grows more rapidly than an undisturbed crystal face.

There are, however, a few phenomena in the crystallization of sucrose where we can observe the occlusion of mother liquor or dark colored impurities in the crystallization process. This is specifically when we are using a dark colored seed sugar and afterproduct sugar from raw sugar mills as seed for the commercial boilings. The formation of these dark colored

crystals occurs specifically in low product boilings. It can be found, not as an exception, but rather frequently in commercial raw sugars where we can see microscopically the seed crystals as a dark center in the final product⁷.

It can be observed in a careful examination of raw sugar crystals that a dark colored layer is present in the inside of the crystal making the impression that a layer of mother liquor has been formed around a part of a grown sucrose crystal with deposition of sucrose over the molasses layer. In an enlarged and schematic form the picture is given in Fig. 5/3.

This phenomenon occurs particularly when a *C*-sugar in canesugar mills has been used as seed for the commercial boilings, the *C*-sugar having an imperfect surface as a result of washing or poor circulation, resulting in dissolution and growth of the crystals circulating in the pan.

As far as our practical experience goes, it is found particularly when, for some reason or another, a strike during its build up has been interrupted in the crystallization process with superheating of a part of the massecuite. It is not a result of washing a *C*-sugar in a magma mixture with water or clarified juice; but the origin of this abnormality must be found during the crystallization process in the pans.

It has also been found that when a *C*-strike is made on a footing of a mixture of syrup and *A*-molasses of lower purity, resulting in sucrose crystals of great uniformity and regularity, the tendency for a formation of a colored nucleus originating from the *C*-sugar used as seed for the commercial boilings is much less than when an irregular footing has been used made on meladura. Contrary to the expectation, it is found that the production of a commercial raw sugar free of this kind of imperfection with the inclusion of a visible amount of molasses is less when the seed has been formed in a medium of low purity than when it has been formed in a medium of high purity.

The inclusion in molasses is probably caused by a local dissolution of the crystal surfaces resulting from washing or overheating in the pans, and when the crystallization of the formed crystals continues, the caves and pockets present on the crystal surface are overgrown by the crystallizing sucrose with an occlusion of mother liquor.

Our present experience indicates that the assumption that a cleaner crystal would result if the footing for *C*-boilings is made with pure syrup instead of using *A*-molasses or a mixture of *A*-molasses and syrup, is not based on practical observations. To the contrary, available facts show that the cleanest sugar, free of visible inclusions, is made when the sugar is crystallized in a medium of low purity, guaranteeing a great uniformity of

the crystals and formed at a slower rate of growth than in a high purity medium. It is the combination of the lattice of the sucrose crystal, its stability against temperature differences, and the dissolving action when the surrounding mother liquor for some reason or another becomes undersaturated which regulates how far the original crystal is able to correct, without any inclusions, its original form.

The inclusion of dark colored impurities in sugars occurs mostly in the last phase of the boiling of *C*-strikes and specifically with a poor circulation and great temperature differences in the circulating massecuite when we have a local undersaturation at the places of highest temperature specifically when the massecuite is moving slowly through the heating elements of the calandria.

We are dealing here probably with a typical inclusion of mother liquor in cavities and grooves formed in a medium of high viscosity and low purity, which cavities are filled up with mother liquor and are overgrown in the following phase of the boiling process when the crystals are exposed to a highly supersaturated solution.

There are also indications that the nature of these inclusions is not only pure mother liquor but that we are dealing with absorbed nonsugars, specifically the group of nonsugars described in the literature as melanoidins.

When the *C*-sugars of factories where this phenomenon of a dark colored *C*-sugar is observed are washed with a saturated sugar solution and dissolved, it is found that the impurity of a washed *C*-sugar can never be brought higher than 97 to 98. When the color concentration of these nonsugars is determined and expressed per 100 nonsugars, the color concentration of these nonsugars can be more than double that of the final molasses. Whether we are dealing here with the adherence of dark colored impurities in a colloidal state to a crystal surface and that these colloidal impurities are overgrown is a subject which must be investigated before we are able to give a definite answer. But it is certain that in boiling *C*-massecuites, we are dealing with nonsugars and conditions of crystallization fundamentally different from what we find in the crystallization of syrup or *A*-molasses which have not been subjected to the same high concentrations and temperature conditions as found in final boilings.

The bad reputation of molasses adhering to *C*-sugar with practically every sugar technologist has undoubtedly a good reason because molasses adhering to *C*-sugar is of a much more detrimental character for good crystallization than nonsugars as found in the virginal raw materials in sugar factories.

8. Effect of Precipitated Nonsugars on the Purity of Centrifuged Sugar

In the preceding paragraphs we have stressed the point that different groups of nonsugars become insoluble and are precipitated during the crystallization process.

The elimination of these precipitated nonsugars from the centrifuged sugars is extremely difficult because the centrifugal process has the character of a filtration process where the sugar acts as filter aid and is holding back the precipitated impurities. This accumulation of precipitated impurities is well known. It is, for instance, a common experience that some of the suspended matter present in canesugar mills in the syrup is found exclusively in *A*-sugar. This is, for instance, the case with fine bagacillo which is found exclusively in *A*-sugar and which is removed completely in the centrifugal process with the commercial *A*-sugar. *B*-sugar is free of bagacillo.

It is also found that some of the lipids described as waxy material are present to a greater extent in *A*-sugar than in *B*-sugar. But on the other hand, when it comes to precipitated and insoluble impurities, *B*-sugar contains more silicic acid, fosfates and calcium salts combined with all kinds of organic acids.

As to the effect on the filtrability of sugar, it is usually found that the coarser precipitated and suspended nonsugars present in *A*-sugar do not affect the filtrability per unit of suspended nonsugars to the same extent as those present in *B*-sugar.

Contrary to what has been stated, it is sometimes found that an *A*-sugar higher in lipids than the corresponding *B*-sugar has a much better filtrability than the *B*-sugar. There does not exist a simple relation between the filtrability of a sugar and its lipid content.

The worst product for filtration is *C*-sugar. Although sometimes it has been found that the lipid content of *C*-sugars is low, the calcium content as insoluble impurity it always high.

The statements on the relationship between the filtrability of sugar and suspended matter have practically always been oversimplifications or are nothing else than assumptions. The worst impurities in their effect on filtrability of sugar are the different types of nonsugars precipitated during the crystallization process and specifically the nonsugars precipitated in *B*- and *C*-boilings. Most of these nonsugars are very complex compounds of calcium-polymolecular-acidic nonsugars formed as decomposition products during the boiling process, combining with calcium and forming insoluble precipitates in extremely fine dispersion.

Practical research of sugar technology has to give attention to the nature, solubility, formation and polymerization of this group of nonsugars. All the practical endeavors to manufacture raw sugar with a good filtrability must be based on the prevention of this precipitation, respectively on the elimination of this group of nonsugars.

Practical experiments done for the removal of these precipitates in *A*- and *B*-molasses by diluting this molasses and using fosfatation, filtration over kieselguhr and centrifugation have shown a great improvement of the quality of the sugar. But these practices could never become generally adopted up till now by lack of economic justification for the introduction of the same.

The improvement that can be made in the manufacture of raw sugars with a low content of insoluble impurities, respectively a good filtrability has not yet found simple expressions for the evaluation of these characteristics from a refiner's point of view. The difficulty is that the amount of suspended matter is not an expression for the refining characteristics of raw sugar. There are suspended nonsugars which are of no disadvantage at all to the refiner as, for instance, fine bagacillo. This can be easily removed by filtration. We have to start with a differentiation for the different types of insoluble impurities either by chemical or by physical methods, and increase our knowledge about the removability and the practical effects they have on the technological processes in the refinery.

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CHAPTER 6

CONTROL METHODS AND EQUIPMENT IN SUGAR CRYSTALLIZATION

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1. Introduction

The crystallization process is one of the most important steps in the commercial manufacture of cane and beet sugars, both raw and refined. Recognition of this has prompted a great deal of research and investigative work in the theory and practice of sugar crystallization.

From a practical standpoint, efforts have been directed primarily toward the development of suitable techniques, control methods, and instruments which will permit obtaining uniform size grain of good quality, with maximum yield. This chapter will be limited to a discussion of methods and equipment for controlling crystallization. The principles and techniques are covered in other chapters in this volume.

There is much published literature available on the general subject of crystallization and also on the specific aspect of sugar boiling control. Reference may be made to such writings for more details than can be included herein.

2. Development of Control Methods

In the early manufacture of sugar, crystallization was allowed to take place spontaneously. Sugar boiling was an art and the sugar boiler learned from experience how to control boiling conditions so that reasonably good crystals were obtained. There were few instruments available and indicating thermometers and vacuum gages were largely relied upon for control purposes.

Over sixty years ago CLAASSEN¹ pointed to the need for a better means of controlling the crystallization process. He emphasized that supersaturation must be controlled to obtain uniform crystal formation and growth. The degree of supersaturation maintained should be such that crystals could

grow with sufficient rapidity, but not so great as to allow formation of new grain. CLAASSEN showed that the concentration of a boiling sugar solution was related to its boiling point elevation. He presented tables which permitted converting boiling point elevation to supersaturation.

Early investigators attempted to develop an instrument for measuring supersaturation directly, but were not successful. One of the first instruments used in sugar boiling was the brasmoscope developed by CURIN². This consisted of a thermometer placed alongside a barometer. From the temperature and vacuum, boiling point elevation could be calculated and expressed as concentration by reference to tables. CLAASSEN³ later modified the device.

In 1909 a German patent was issued to LANGEN⁴ on a device for measuring boiling point elevation. It represented an advancement in that it measured boiling point elevation directly without the necessity of calculations. The device utilized a thermo-element, one junction of which was located in the boiling massecuite and the other in boiling water kept at the same vacuum as the massecuite. LANGEN's device was an improvement over the brasmoscope but only indicated boiling point elevation of the mother liquor and not supersaturation. The limitations of these early instruments are well explained by THIEME⁵, HOLVEN⁶ and others.

Other early investigators applied refractometric methods utilizing the Zeiss sugar pan refractometer to measure concentration. However, this did not have wide application because of difficulty in obtaining consistently accurate readings. Use of conductivity equipment such as the cuitometer was also investigated rather widely. The latter subject is discussed in another chapter in this volume.

About 25 years ago, attention was directed more actively to the entire field of methods and techniques for obtaining improved control over sugar boiling operations. KUCHARENKO⁷ emphasized the need for developing a device for direct measurement of supersaturation. During intensive studies of crystallization, BERGH⁸ developed a means for automatic pressure regulation in conjunction with SHIELDS⁹. WEBRE^{10, 11} also carried on studies relating to pan design and the use of pan control instruments. In recent years, GILLET¹² made extensive investigations and developed excellent techniques of sugar boiling. His work and that of WEBRE have contributed much to the scientific and practical principles of sugar crystallization.

In 1933 SMITH^{13, 14} developed a system of vacuum pan control and described an instrument for measuring and recording boiling point elevation. SMITH's device represented a forward advance and gave a reasonably good measure of boiling point elevation. However, it did not measure supersaturation.

In 1936, HOLVEN¹⁵ discovered the influence of absolute pressure on supersaturation and subsequently, a means for directly measuring supersaturation⁶. A few years ago, PRICE¹⁶ and HALL¹⁷ described a commercial supersaturation instrument based on HOLVEN's patents as adapted by the Brown Instrument Division of Minneapolis-Honeywell Regulator Company. COLE¹⁸ is another investigator who worked with supersaturation measurements in crystallization of beet sugars. GENIE¹⁹ has developed modified supersaturation equipment in Belgium.

3. Importance of Control Equipment

Practically all present day authorities recognize that for optimum results it is necessary to have accurate and reliable means for measuring and controlling operations during the various stages of the boiling process. As improved equipment has become available over the years, crystallization techniques have been improved. It is now generally accepted that there is need for three principal controls during the boiling operation, *i.e.*, control of absolute pressure, control of supersaturation, and control of fluidity. The discussion which follows indicates the importance of these more clearly.

In boiling white sugar, for example, a pan is charged with a high density sugar liquor in sufficient quantity to cover the calandria or the lower coils, as the case may be. With the pan under vacuum, the steam is turned on and water evaporated until a predetermined supersaturation is reached. At this point the pan is grained. The exact supersaturation value for grain formation depends upon the method of graining used, *i.e.*, whether by spontaneous formation, by shocking, or by seeding. Modern methods involve shock-seeding with a small amount of very fine sugar particles such as powdered or dry fondant sugar. This is usually done at relatively low supersaturation values in the metastable zone. In this zone the crystals introduced will grow but practically no new crystals will form. Higher supersaturations in the so-called labile zone are avoided to prevent spontaneous grain formation which would result in non-uniform grain size and poor grain quality. In shock-seeding white sugar strikes, authorities consider a safe top supersaturation limit to be about 1.4. Higher values may be used for lower purity boiling materials.

Because supersaturation is so critical during grain formation, the importance of having some means of indicating or measuring supersaturation is obvious. It is further important to control supersaturation during the early growth period of the grain. If the supersaturation becomes too low, some of the grain may dissolve – and if too high, new grain may form.

Regardless of how the point of grain formation is determined in the boiling cycle, it is essential that absolute pressure be accurately controlled. Lack of control results in temperature variations that cause changes in supersaturation. If the pressure rises, the temperature increases and grain is apt to be melted. If the pressure drops, the temperature will drop and could result in new grain or conglomeration. Sudden pressure changes also slow down or speed up boiling.

After the grain is formed and established, the boiling process becomes one of growing the crystals to the proper size. This involves feeding liquor to the pan at a proper rate. During these later stages supersaturation measurements with present equipment are not accurate because of the effect of hydrostatic head on the response of the pan thermometer. On the other hand, the fluidity of the massecuite becomes of importance. Measurement of fluidity can be used to control liquor feed. Such a measurement is of particular value at the end of the strike, as it is desirable to drop it as 'tight' as possible in order to obtain maximum yield. In view of this, the third control of importance, in addition to supersaturation and absolute pressure, is that of fluidity or consistency of the massecuite.

Even with these different controls, the need for effective techniques becomes increasingly obvious when it is recognized that there are innumerable other variables. Techniques must be varied depending on the purity of the syrup or sugar liquor being boiled. The nature of impurities varies with different types of solutions and affects grain formation, rates of crystallization, etc. Pan characteristics have an important effect and cause variations due to design. Conditions vary depending on whether the pan is a coil or calandria pan, whether mechanical circulation is provided, etc. Steam flows and pressures will differ and affect rates of evaporation. All of these factors must be taken into account in developing proper techniques for each condition encountered. This makes it all the more essential that suitable measuring and control equipment be available.

The general principles of crystallization and the importance of control methods and equipment are discussed in various texts such as GILLET¹², SPENCER-MEADE²⁰, LYLE²¹, BARDORF and BALL²², and others.

4. Basic Data and Definitions

The design of accurate and reliable control instruments requires that precise data be available on the fundamental properties of sugar solutions. Some of the more important properties are solubility, boiling point elevation, and supersaturation. Data should be available for pure sucrose solutions

and also for impure sugar solutions at various temperatures and absolute pressures.

(a) *Solubility of Pure Sucrose*

The amount of pure sucrose that can be dissolved in water increases with temperature. The exact solubilities have been determined by different investigators. HERZFELD's data²³, which were first published in 1892, are based on determinations at six different temperatures. His table of solubilities^{24, 25} has been generally accepted by the sugar industry for many years. However, other investigators in this field agree that it is in error at a number of temperatures. A comparison with more recent solubility data indicates that the Herzfeld values are about 0.3% to 0.4% solids low at 70° C and above, about 0.5% solids high at room temperature, and are low again near 0° C.

Among the newer and more accurate solubility data are those of TAYLOR²⁶ published in 1947. These values are based on actual determinations in the range of 64–82° C. COLE¹⁸ used these data and obtained values at other temperatures by extrapolation.

The latest data available are those determined by CHARLES²⁷ in 1958. These are based on determinations over the temperature range of 0–90° C. They compare well with values obtained over the more restricted ranges by TAYLOR and others.

The equations used by these three investigators are as follows:

$$\text{HERZFELD} \quad C = 64.18 + 0.1348 t + 0.000531 t^2$$

$$\text{TAYLOR} \quad C = 63.608 + 0.133 t + 0.000722 t^2$$

$$\text{CHARLES} \quad C = 64.407 + 0.07251 t + 0.0020569 t^2 - 9.035 \times 10^{-6} t^3$$

where

$$C = \% \text{ sucrose at saturation}$$

$$t = \text{temperature, } ^\circ\text{C}$$

Table 1 shows a comparison of the solubility of pure sucrose over the temperature range of 0–90° C as given by these three investigators.

A great deal of work on solubility of sucrose solutions has been done by other investigators over the years. These include GRUT²⁸, D'ORAZI²⁹, HRUBY and KASJANOV³⁰, DUNNING, EVANS and TAYLOR³¹, WISE and NICHOLSON³², KELLY³³ and others.

(b) *Solubility of Impure Sugar Solutions*

Accurate data for solubilities of impure sugar solutions are not available because of the large variation with different types of impurities. The effect

of various organic and inorganic impurities as well as sugars other than sucrose has been generally recognized. As a result, considerable work has been done in this field in determining the effect of different salts, invert sugar, etc. However, as the composition of different impure sugar solutions varies, it is generally necessary to determine the solubility for each specific type of solution.

TABLE 1
SOLUBILITY OF PURE SUCROSE IN WATER

Temp. (° C)	% Sucrose by weight			Grams sucrose per 100 grams water		
	HERZFELD 1892	TAYLOR 1947	CHARLES 1958	HERZFELD	TAYLOR	CHARLES
0	64.18	—	64.41	179.2	—	181.0
5	64.87	—	64.82	184.7	—	184.3
10	65.58	—	65.33	190.5	—	188.4
15	66.34	—	65.93	197.1	—	193.5
20	67.09	—	66.61	203.9	—	199.5
25	67.89	—	67.35	211.4	—	206.4
30	68.70	(68.22)	68.19	219.5	(214.7)	214.4
35	69.55	(69.12)	69.08	228.4	(223.8)	223.4
40	70.42	(70.05)	70.02	238.1	(233.9)	233.6
45	71.32	(71.02)	71.01	248.7	(245.1)	245.0
50	72.25	(72.02)	72.05	260.4	(257.4)	257.7
55	73.20	(73.06)	73.11	273.1	(271.2)	272.0
60	74.18	(74.15)	74.21	287.3	(286.8)	287.8
65	75.18	75.25	75.33	302.9	304.0	305.4
70	76.22	76.40	76.46	320.5	323.7	324.9
75	77.27	77.58	77.60	339.9	346.0	346.4
80	78.36	78.81	78.75	362.2	371.8	370.5
85	79.46	(80.06)	79.88	387.0	(401.5)	397.0
90	80.61	(81.35)	81.01	415.7	(436.3)	426.5

Note: Figures in parenthesis extrapolated by COLE¹⁸.

CLAASSEN¹ published solubility data quite a few years ago for sugar beet juices in Europe. PRINSEN GEERLIGS³⁴ determined solubilities using cane juices in Java. VAN DER LINDEN³⁵ and JACKSON and SILSBEE³⁶ investigated the solubility of sucrose in the presence of invert sugar and found there was a mutual influence on their respective solubilities. THIEME⁵ discussed this subject in considerable detail and presented data for cane juices from Java. Other investigators who have studied the effect of impurities on solubilities of cane and beet solutions include KUCHARENKO and ROZOVSKY³⁷, BROWN and NEES³⁸, NEES and HUNGERFORD³⁹, VANHOOK and SHIELDS⁴⁰, VANHOOK⁴¹, and RORABAUGH and NORMAN⁴².

These investigators have shown the effect of various impurities on solubility of sucrose, and particularly that sucrose is more soluble in the

presence of beet impurities than in the presence of cane impurities. Also, it has been shown that high ash content tends to increase sucrose solubility.

(c) *Saturation Coefficient*

This expression is often used as a measure of solubility of impure solutions. It is the ratio of the solubility of pure sucrose in water in the presence of impurities, to its solubility in the absence of impurities. It may be expressed by the following formula:

$$C_{T,P} = \frac{(S/W)_{T,P}}{(S/W)_{T,100}}$$

where:

- $C_{T,P}$ = saturation coefficient at temperature T and purity P
- $(S/W)_{T,P}$ = sucrose-water ratio for a saturated solution at temperature T and purity P
- $(S/W)_{T,100}$ = sucrose-water ratio for a saturated solution at temperature T and 100 purity (see Table 1, last three columns).

(d) *Boiling Point Elevation – Pure Sucrose Solutions*

The boiling point elevation, also called boiling point rise, is defined as the temperature difference between the boiling point of a sugar solution at a

TABLE 2
BOILING POINT ELEVATION OF PURE SUCROSE SOLUTIONS (HOLVEN)

Grams sucrose per 100 grams water	% Sucrose by weight	Vapor temperature (° C)						
		100	80	70	60	50	40	30
		Boiling point elevation (° C)						
900	90.00	19.6	18.7	18.3	17.8	17.4	16.9	16.5
800	88.89	17.9	17.0	16.6	16.2	15.8	15.4	15.0
700	87.50	16.0	15.2	14.8	14.4	14.0	13.6	13.2
600	85.71	13.7	13.0	12.6	12.3	12.0	11.6	11.2
500	83.33	11.6	10.9	10.6	10.3	10.0	9.7	9.4
400	80.00	9.4	8.9	8.6	8.3	8.1	7.8	7.5
300	75.00	7.0	6.6	6.3	6.1	5.9	5.7	5.4
200	66.67	4.2	3.9	3.8	3.6	3.5	3.3	3.2
100	50.00	1.8	1.6	1.5	1.4	1.3	1.3	1.2

given absolute pressure and the boiling point of water at the same absolute pressure. Early workers recognized that boiling point elevations varied with sucrose concentration and also with the type and quantity of impurities in the case of impure solutions. CLAASSEN's data¹ developed in 1904 were used by the industry for years to obtain supersaturation values.

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In 1936, HOLVEN¹⁵ questioned these data because the effect of absolute pressure was not taken into account, and pointed out that CLAASSEN's data were valid only at substantially atmospheric pressure. HOLVEN published data on boiling point elevation of pure sucrose solutions at varying pressures. These are shown in Table 2. The values are based on actual determinations at atmospheric pressure. At the lower pressures the values were calculated.

SPENGLER, BOTTFER and WERNER⁴³ made new tests in 1938 and actually determined the boiling point elevation of both pure and impure sugar solutions at different concentrations under various absolute pressures. Their data for pure sucrose solutions as expanded by the U.S. National Bureau of Standards⁴⁶ and by COLE¹⁸ are shown in Table 3.

The data in these two tables are in fairly good agreement at atmospheric pressures. However, at the lower pressures encountered in sugar boiling, considerable differences occur, and HOLVEN's data are higher. For example, at 40° C vapor temperature the difference is as much as 4.2° C.

Other investigators who have reported on boiling point elevation data

TABLE 3

BOILING POINT ELEVATION OF PURE SUCROSE SOLUTIONS (COLE)

(From data of SPENGLER, BOTTFER and WERNER⁴³ as expanded by U.S. National Bureau of Standards⁴⁶ and by COLE¹⁸)

Grams sucrose per 100 grams water	% Sucrose by weight	Vapor temperature (° C)							
		100	90	80	70	60	50	40	30
		Boiling point elevation (° C)							
1000	90.91	20.70	19.38	18.16	16.93	15.79	14.71	13.68	12.70
900	90.00	19.27	18.04	16.91	15.76	14.70	13.70	12.73	11.82
800	88.89	17.69	16.56	15.52	14.47	13.50	12.57	11.69	10.85
700	87.50	15.93	14.92	13.98	13.03	12.15	11.32	10.53	9.77
600	85.71	13.98	13.09	12.27	11.44	10.67	9.94	9.24	8.58
500	83.33	11.81	11.06	10.36	9.66	9.01	8.39	7.80	7.24
400	80.00	9.44	8.84	8.27	7.72	7.20	6.71	6.24	5.79
300	75.00	6.88	6.44	6.02	5.63	5.25	4.89	4.55	4.22
200	66.67	4.25	3.98	3.72	3.48	3.24	3.02	2.81	2.61
100	50.00	1.79	1.68	1.57	1.46	1.37	1.27	1.18	1.10
50	33.33	0.74	0.69	0.65	0.61	0.56	0.53	0.49	0.45

include TRESSLER, ZIMMERMAN and WILLITTS⁴⁴, and OTHMER and SILVIS⁴⁵.

The best available data at present appear to be those of SPENGLER *et al.*, since they are based on recent laboratory determinations of boiling point elevation at varying pressures. The data have also been published by the U.S. National Bureau of Standards⁴⁶.

(e) *Boiling Point Elevation – Impure Sugar Solutions*

Boiling point elevations for low purity cane sugar solutions from Java have been reported by THIEME⁵. HOLVEN used these data in developing his supersaturation relationships. In his book on *Low Grade Sugar Crystallization*, E. C. GILLET¹² includes a series of graphs showing the boiling point elevation at different absolute pressures, purities and supersaturation values. The values determined by SPENGLER and associates are shown in the reference previously mentioned⁴³.

As in the case of pure sucrose solutions, the data from those two sources likewise differ for impure sugar solutions. The boiling point elevations differ not only because of different methods of determination but also because of variations in the nature of impurities in the solutions. These variations occur between cane and beet sugars and also between the same type of sugar produced in different areas. As a result, it is not possible to report values of boiling point elevations for impure sugar solutions which are generally applicable throughout the sugar industry.

(f) *Supersaturation – Pure Sucrose Solutions*

The most widely used definition of supersaturation is that originally proposed by CLAASSEN¹ and later applied by HOLVEN⁶ and others. The expression 'supersaturation coefficient' is equal to the sucrose/water ratio for a given solution divided by the sucrose/water ratio for a saturated solution of the same purity and temperature. Expressed by formula, this becomes:

$$\text{Supersaturation} = \left(\frac{S/W}{S_1/W_1} \right)_{P,T}$$

where

S/W = sucrose/water ratio for a solution of purity P and temperature T

S_1/W_1 = sucrose/water ratio for a saturated solution of purity P and temperature T .

Other definitions of supersaturation have been offered. In HONIG⁴⁷, G. W. PAYNE mentions two ways of expressing supersaturation which are similar to the above.

HOLVEN⁶ discovered a mathematical straight-line relationship between supersaturation and boiling point elevation for various absolute pressures which permitted direct measurement of supersaturation. Prior to this it had always been necessary to calculate supersaturation by reference to tables

or graphs. This relationship has been confirmed by others, and COLE¹⁸ gives a good up-to-date explanation.

The supersaturation relationships, of course, depend on the basic data used for solubilities and boiling point elevations, and on variations in absolute pressure. The supersaturation charts developed by HOLVEN have

TABLE 4

BOILING POINT ELEVATION FOR PURE SUCROSE SOLUTIONS AT VARIOUS SUPERSATURATION VALUES AND VAPOR TEMPERATURES (FROM HOLVEN)

Supersaturation	Vapor temperature °C			
	50	60	65	70
Boiling point elevation				
0.6	2.6	3.2	3.6	4.0
0.8	4.0	4.7	5.3	5.8
1.0	5.3	6.3	7.0	7.6
1.2	6.7	7.9	8.8	9.4
1.3	7.4	8.9	9.6	10.2
1.4	8.1	9.5	10.4	11.1
1.6	9.8	11.2	12.0	12.9
1.8	10.8	12.8	13.7	14.6
2.0	12.1	14.2	15.3	16.3

been generally accepted by the sugar industry. These have been modified recently as outlined by PRICE¹⁶, by using the more recent solubility data of TAYLOR²⁶ and boiling point elevation data of SPENGLER and associates⁴³.

The boiling point elevation for pure sucrose solutions at various supersaturations and vapor temperatures, as reported by HOLVEN⁶, are shown in Table 4. Those reported later by COLE¹⁸ and based on the data of TAYLOR

TABLE 5

BOILING POINT ELEVATION FOR PURE SUCROSE SOLUTIONS AT VARIOUS SUPERSATURATION VALUES AND VAPOR TEMPERATURES (FROM COLE)

Supersaturation	Vapor temperature (° C)				
	50	60	65	70	80
Boiling point elevation					
0.6	2.26	2.81	3.15	3.57	4.63
0.8	3.27	4.06	4.56	5.15	6.71
1.0	4.32	5.36	6.01	6.79	8.86
1.2	5.39	6.68	7.48	8.44	10.98
1.3	5.92	7.33	8.21	9.25	12.02
1.4	6.46	7.98	8.93	10.05	13.03
1.6	7.50	9.24	10.32	11.59	14.94
1.8	8.52	10.45	11.64	13.03	16.72
2.0	9.49	11.60	12.89	14.41	18.34

and of SPENGLER and associates are shown in Table 5. Others who have studied supersaturation values are HONIG and ALEWIJN⁴⁸, SILIN⁴⁹, and DUBOURG, SAUNIER and LEMAITRE⁵⁰.

(g) *Supersaturation – Impure Sugar Solutions*

The supersaturation-boiling point elevation relationship for impure sugar solutions, as mentioned earlier, is influenced by the type and quantity of non-sucrose materials. This occurs because both the solubility at saturation and the boiling point elevation at a given concentration are influenced by the impurities present. The effect of these impurities can usually be compensated for in boiling white cane sugars, because the variation from 100° purity is small and the nature of the impurity is relatively constant. In lower purity material such as raw beet and cane juices and remelt sugar liquors, such compensation is not always adequate. Purity correction must therefore be determined for each individual situation.

Because of the variations caused by these impurities, no specific data are included herein. The only readily available supersaturation data for impure sugar solutions are those developed by HOLVEN⁶ for cane sugars and published by E. C. GILLET¹².

5. Pan Control Equipment

Types of instruments and control devices vary on different pan installations. These differ in principle and manufacturer. However, they are generally all directed toward the same objective of providing suitable means for controlling crystallization in accordance with carefully developed techniques.

In general most pans are equipped with certain basic instruments. These usually include a gage for indicating steam pressure, a vacuum or absolute pressure gage, an indicating or recording thermometer for pan temperature, and some type of low power microscope for observing crystal size and structure.

In addition to these standard devices, special control equipment of some type is desirable for best operation, as previously mentioned. These are described in some detail in the succeeding sections.

(a) *Control of Absolute Pressure*

As previously pointed out, control of absolute pressure is essential for proper boiling. Vacuum measurements are generally not accurate enough

for this purpose because of variations in barometric pressure. Modern controls are therefore based on absolute pressure.

For purposes of indication, absolute pressure gages of the mercury column type are normally used. The scale must be accurate and the gage carefully calibrated. Suitable gages calibrated to 0.1 inch of mercury absolute pressure are commercially available from various instrument manufacturers. Similar gages calibrated in centimeters of mercury are also obtainable.

In addition to indicating gages, means are required to control the absolute pressure. This is generally accomplished by regulating the flow of water to the pan condenser. One system that has been used successfully is that devised

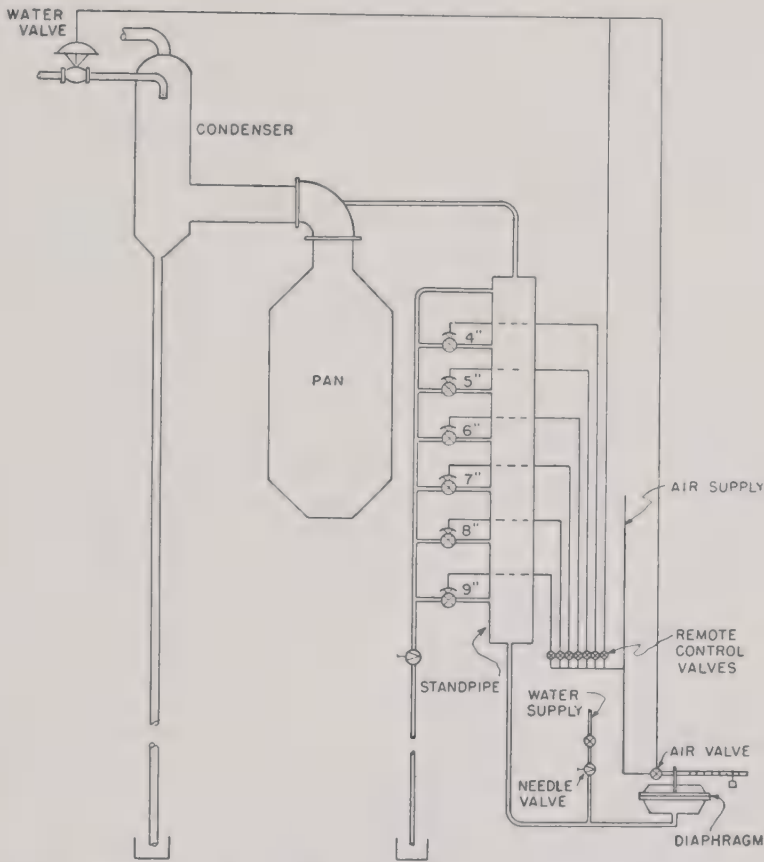


Fig. 6/1. Absolute pressure regulator system for vacuum pan.

by SHIELDS⁹ some years ago, and modified by BERGH⁸. Fig. 6/1 shows a diagrammatic sketch of this control system.

Commercial absolute pressure recorder-controllers are now available from most of the major instrument companies. These provide more accurate control than older types of straight proportioning controllers. They can be

equipped with proportional, automatic reset and derivative types of control action as desired. In addition, program control can be provided whereby a cam and follower act to change the pressure automatically in accordance with a predetermined time cycle.

(b) *Measurement of Boiling Point Elevation*

As mentioned previously, the measurement of boiling point elevation has been used to give an indication of concentration and thereby provide a means for improved graining control. This type of instrument is not direct reading in terms of supersaturation but only gives the difference in two temperatures. The principle may be expressed by the following formula:

$$\text{B.P.E. (Boiling Point Elevation)} = T_s - T_w$$

where

T_s = boiling point of the sugar solution

T_w = boiling point of water at the same absolute pressure.

In spite of their limitations, instruments based on this principle have received sufficient use in recent years to warrant a brief description.

Resistance thermometers are used to measure temperatures. One thermometer is generally located in the center well of the vacuum pan to give a measure of the temperature of the boiling material. A second thermometer is located in a small boiling water pot generally called the pilot pan, which has a pipe connection to the vapor space of the vacuum pan. This gives a measure of the temperature of boiling water at the same absolute pressure as in the vacuum pan. By connecting these two resistance thermometers in a temperature-differential recorder, a direct measure of the boiling point elevation is obtained. The recorder can be equipped with control contacts for use in actuating a motor-driven valve on the feed line to the pan in accordance with any selected boiling point elevation.

The device developed by SMITH^{13, 14} used this principle. It was commercialized by the Leeds and Northrup Company of Philadelphia and has been referred to as the 'Micromax Pan Controller'. The Micromax was installed by various sugar factories in Hawaii. According to SMITH, the equipment provided a reasonable good control, but he encountered difficulty because of variations in barometric pressure. Furthermore, as in any similar type of equipment, poor pan circulation caused a sluggish response. However, if absolute pressure is maintained constant, the instrument gives a fairly reproducible indication of the density of the mother liquor.

(c) *Indication and Measurement of Supersaturation*

As indicated earlier, many investigators attempted to devise and apply various means for obtaining measure of supersaturation. Some of the more recent developments were quite successful.

One approach involved calibration of an absolute pressure gage in terms of massecuite temperature for designated supersaturation values. The temperature scale is determined from boiling point elevation tables. The scale shows what the pan thermometer should read for any given absolute pressure to give a pre-established supersaturation value. The scale is adjustable so it can be positioned for any desired supersaturation. An illustration and description of this arrangement is given in E. C. GILLETT's book¹².

Another approach was that developed by WEBRE⁵¹, involving the use of nomographs. These related boiling point elevations at different absolute pressures to supersaturation values. The nomographs had polar coordinates

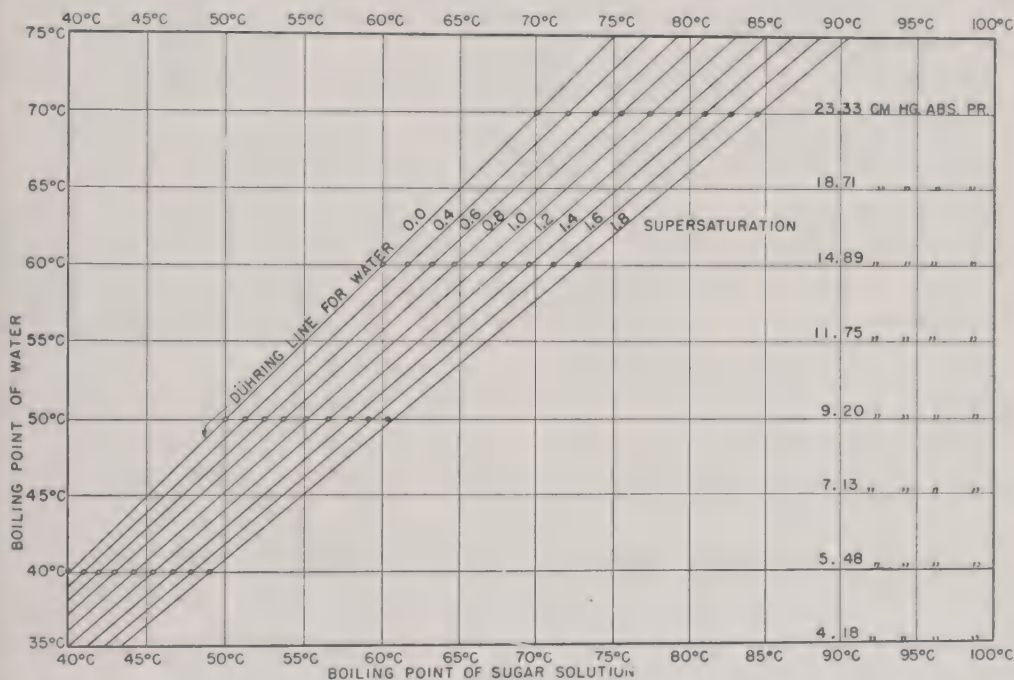


Fig. 6/2. Representative constant supersaturation lines for a sugar solution of 100% purity.

and could be placed on the face of a recording thermometer under the pointer. However, absolute pressure had to be read separately and applied to the nomograph.

The work of HOLVEN⁶, previously referred to, resulted in the first practical means for measuring supersaturation directly. He derived a relationship

between supersaturation and boiling point elevation which, unlike uncompensated boiling point elevation measurements, was independent of the absolute pressure. He found that a plot of the boiling points of sugar solutions of any degree of supersaturation against the corresponding boiling points of water at the same absolute pressures gave a straight line at all pressures usually encountered in sugar boiling. For illustration, constant supersaturation lines for a 100° purity sugar solution are shown in Fig. 6/2. HOLVEN showed that the slope of these lines varied only with supersaturation and the purity of the sugar solution. Mathematically, the above relationship may be expressed as follows for constant purity:

$$\frac{T_w - T_w^1}{T_s - T_s^1} = \tan \theta$$

where

T_s and T_w = the boiling points of the sugar solution and water at the same absolute pressure

T_s^1 and T_w^1 = the corresponding boiling points of the sugar solution and water at some other absolute pressure

$\tan \theta$ = slope of line of constant supersaturation

The relationship may be written in a somewhat simplified form by substituting a constant K for the quantities T_w^1 and T_s^1 . The modified expression is the equation for a family of straight lines of varying slopes

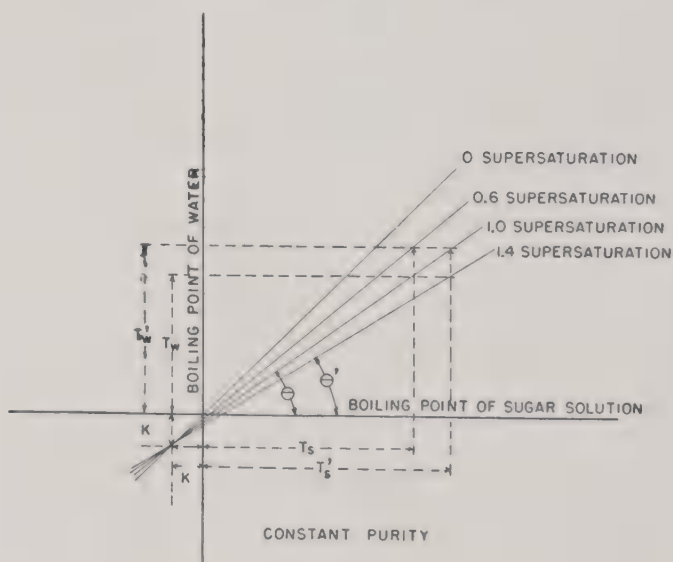


Fig. 6/3. Graph illustrating manner in which constant supersaturation lines intersect at a common point, K .

representative of supersaturation, all intersecting at a common point having the same numerical value for both coordinates (K, K). It is not as exact as the first form of the relationship, inasmuch as K varies with both supersaturation and purity. However, the variation in K with supersaturation is negligible for practical purposes, and the variation with purity can be com-

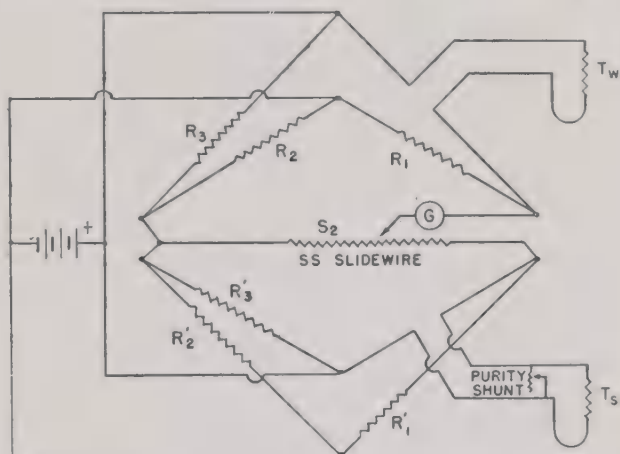


Fig. 6/4. Basic HOLVEN circuit for measurement of supersaturation.

pensated for in a measuring circuit. The general manner in which supersaturation lines intersect at essentially a common point K is shown in Fig. 6/3.

By using the above relationship, HOLVEN devised an instrument using a relatively simple circuit which reads directly in supersaturation values. This instrument, in its original form, consists essentially of two unbalanced Wheatstone bridge circuits connected in opposition through a slide wire potentiometer (see Fig. 6/4). Each bridge contains a resistance thermometer, one of which is installed in the vacuum pan and the other in a pilot pan containing boiling water at the same pressure that prevails in the vacuum pan. The boiling temperatures in the two pans correspond to T_s and T_w , respectively. Provision is made for compensating for the purity of the liquor.

It is important that the thermometers be of such design that they are highly sensitive to temperature changes. At the same time, the pan thermometer must be sufficiently rugged to withstand breakage from the boiling massecuite, since it is normally located in the center of the pan just below the level of the graining charge. Fig. 6/5 shows one type of thermometer before assembly and Fig. 6/6 shows the assembled unit with the heavy metal guard used to protect the thermometer in place. The entire unit is mounted on a long brass pipe which is held in place by brackets and which contains the thermometer cable connecting to the instrument. Fig. 6/7 shows a photo-

graph of the water boiling pilot pan which is connected by a 2" pipe to the vapor elbow of the pan. In some installations, the pilot pan is located on the top shoulder of the vacuum pan. Fig. 6/8 shows the supersaturation recorder. At the right in this picture is the seed cup which may be operated automatically or manually. Fig. 6/9 is a diagrammatic sketch of the general supersatu-

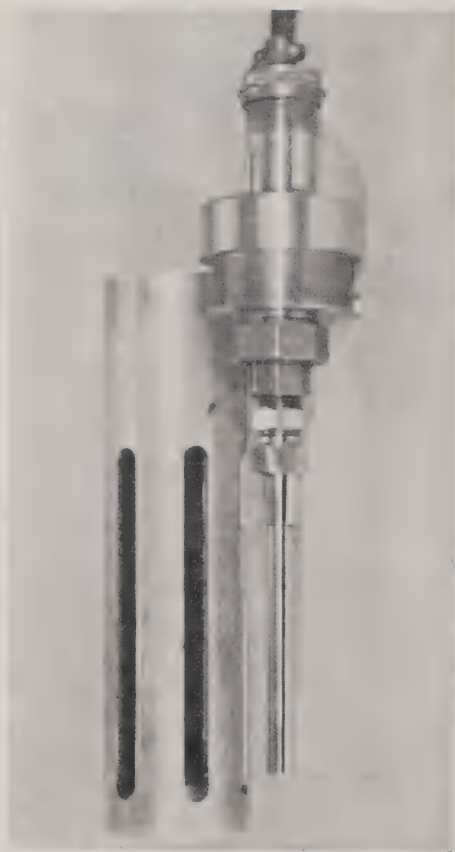


Fig. 6/5. Unassembled resistance thermometer for measuring temperature in vacuum pan.

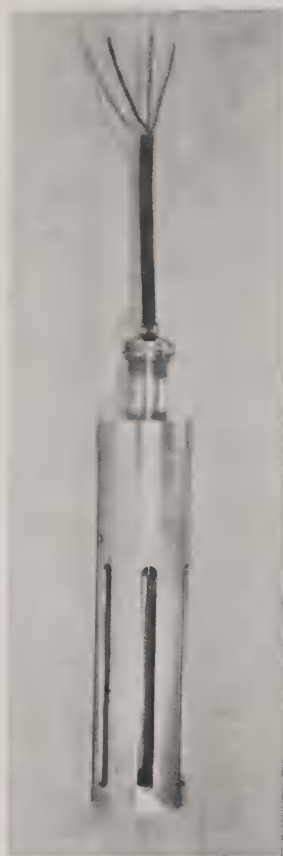


Fig. 6/6. Assembled resistance thermometer.

ration recorder arrangement on a pan. A brief description of this equipment may be found in a previous paper by the author⁵².

As mentioned earlier, the Brown Instrument Division of Minneapolis-Honeywell Regulator Company have secured the patent rights to HOLVEN's invention. They adapted these principles into one of their instruments and now commercially manufacture the Brown Supersaturation Recorder. Fig. 6/10 shows this instrument in the lower right-hand corner. Fig. 6/11 shows the basic circuit.

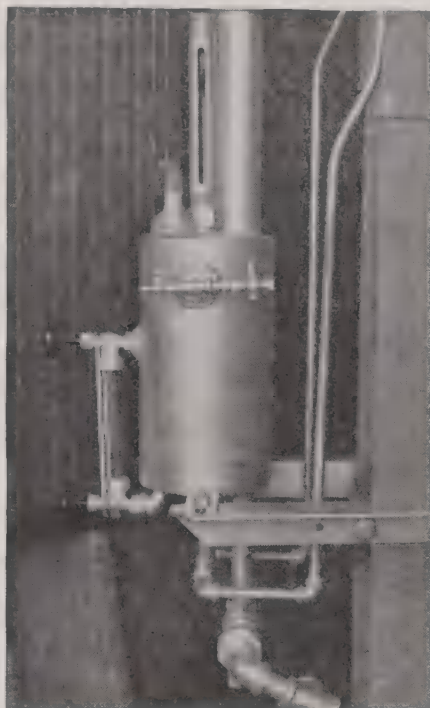


Fig. 6/7. Water boiling pilot pan.

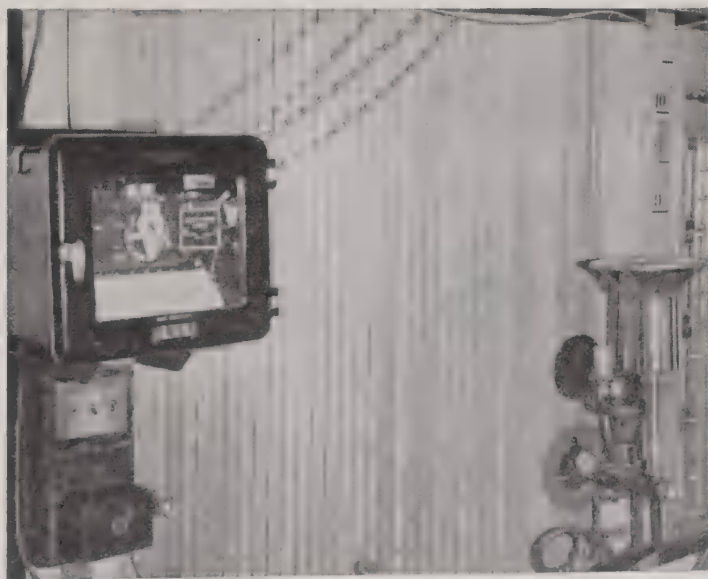


Fig. 6/8. HOLVEN supersaturation recorder.

The equation used to relate boiling point rise to supersaturation in the Brown instrument is as follows:

$$T_x = (T_s + 75) \left(\frac{X(S_s) + 32 - K_s}{7220 Q} \right) - 0.0086$$

where

- T_x = boiling point rise
- T_s = temperature of sugar solution
- X = supersaturation
- S_s = concentration of saturated solution at T_s
- K_s = linearity correction factor at concentration of solution
- Q = purity factor

This equation differs in form from that used in the HOLVEN circuit primarily for ease of circuit design. It also reflects the newer data used in calculating the supersaturation-boiling point elevation relationship.

Using the same general principles of supersaturation measurement, GENIE¹⁹ has recently developed a simplified instrument. A first type was built around a high resistance bridge powered by a stabilized DC source of voltage. A later type uses an electrical circuit composed of a low resistance bridge powered by a low voltage source, and a measuring instrument with crossed coils. This is reported to be less costly than commercial devices and has been used successfully in the Tirlemont Refinery in Belgium.

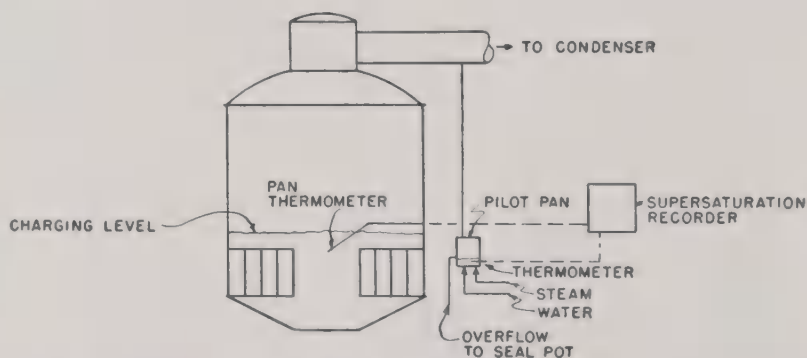


Fig. 6/9. Schematic diagram of supersaturation recorder installation.

(d) *Measurement of Fluidity*

As mentioned previously the fluidity of the massecuite is of importance in sugar boiling. In pans equipped with large mechanical stirrers, the power load on the circulator motor has been used to give a good indication of

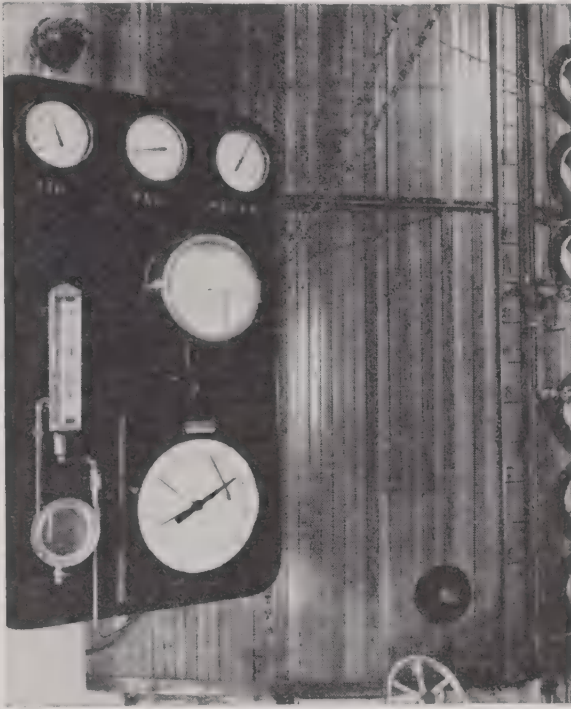


Fig. 6/10. BROWN supersaturation recorder.

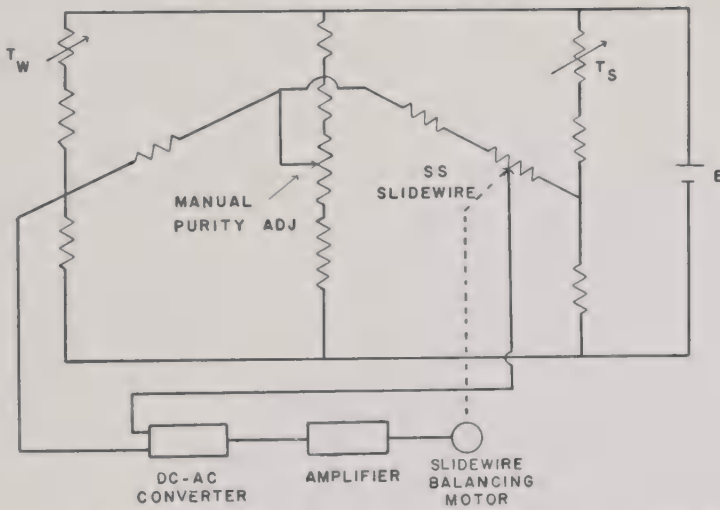


Fig. 6/11. Basic BROWN supersaturation measuring circuit.

fluidity. WEBRE describes a fluidity control for use with his mechanical circulator⁵¹ which has received considerable acceptance. This device utilizes an ammeter connected to the stirrer motor to record fluidity. The ammeter is equipped with a relay which will open or close a valve in the pan feed line. 'Drinks' are fed to the pan as required to maintain constant fluidity.

Recent improvements to this device are marketed by several of the instrument manufacturers including the Minneapolis-Honeywell Regulator Company and the Leeds and Northrup Company. These instruments use a wattmeter to measure power load to the stirrer motor. This eliminates the errors from voltage fluctuations encountered with an ammeter. The motor load is recorded on a standard recorder controller which positions a valve in the pan feed line to maintain constant fluidity. Since these controllers can be equipped with proportional, automatic reset and derivative control, throttling rather than on-off or drink-type of control can be used. These newer controllers have been found to be very effective for automatic control of pan feed.

For pans which are not equipped with circulators, measurement of fluidity is somewhat more difficult. Some investigators have attempted to use a small propeller or rotor located inside the wall of the pan. These are connected to a motor and the torque or power load on the motor is measured and related to fluidity. However, in general these tend to measure the fluidity in a localized area and are not always indicative of conditions throughout the pan. This becomes particularly serious if pan circulation is poor.

A recent commercial consistency indicator and controller for pans without circulators is described in a recent article in *Sugar*⁵³. This is known as the Baikow-Nilsson TORCON. It consists of a rotating paddle driven at constant speed by a synchronous fractional horsepower motor. The mechanism measures the torque required to turn the paddle at constant speed. It is claimed the instrument accurately indicates conditions within the pan and can be used for controlling the feed valve automatically.

Another application of this type of control is that being used at the Savannah Sugar Refinery⁵⁴. This employs a motor-driven rotating element with several small eight-bladed bronze impellers mounted on a shaft. The shaft is driven by a variable-speed quarter-horsepower motor. Adjacent blades of the propeller are of opposite hand to avoid thrust. The motor is mounted in trunnions so that the stator is free to rotate about the shaft. A beam attached to the stator holds weights which counterbalance the torque developed by the impellers.

As the consistency of the massecuite increases, the motor is overbalanced, tripping an air pilot to open the feed valve. The weights are fixed and the control point is varied by changing the speed of the motor. In later versions of this instrument, the counterweight balancing mechanism has been replaced with a standard, force-balance type pneumatic transmitter. This results in a continuous output signal proportional to consistency which can be used by a commercial pneumatic controller.

Other controls have been described by EISNER⁵⁵ and JANSSE⁵⁶. These utilize rate of heat transmission between two points in the pan as a measure of fluidity. When the strike is very liquid, these instruments register high heat transmission rates. As density increases and fluidity decreases, heat transfer and circulation will reverse accordingly.

(e) *Measurement of Massecuite Level*

Measurement and recording of massecuite level in a vacuum pan sometimes is desirable, particularly when strikes are carried above the level of the top sight glass. Pan level measurements can be accomplished satisfactorily with a differential pressure transmitter manufactured by the Taylor Instrument Company, Foxboro Company, and other instrument manufacturers. The transmitter consists of a small diaphragm which can be mounted in the bottom of the pan, preferably in the feed connection. The head of massecuite exerts a pressure on one side of the diaphragm and is balanced by an air pressure on the other side. The balancing pressure is increased or decreased automatically to prevent appreciable movement of the diaphragm. The difference between this balancing pressure and the pan vacuum is detected by a differential pressure recorder. This difference is proportional to massecuite level, providing massecuite density is constant.

6. Automatic Control Equipment

Some or all of the various instruments described have been combined by different investigators to provide partial or complete control of sugar boiling automatically. Completely automatic operations, however, have not generally been adopted because of economic and instrument limitations.

One control system is that described by WEBRE¹⁰. This system includes automatic absolute pressure control, temperature measurements for determining boiling point elevation, a recording ammeter on the pan circulator for control of fluidity, and other indicating and recording gages and instruments. Certain features of this control have been used widely in the United States, Cuba, Puerto Rico and other parts of the sugar world.

Pan control has been developed to a considerable extent in Hawaii. A system installed by C. J. FLEENER at the Oahu Sugar Company some years ago is described by FABIUS⁵⁷. This method used boiling point elevation measurements to control the density of the massecuite through regulation of the feed. Absolute pressure control was also provided. Various other instruments were included. In a more recent report in 1956, GAY⁵⁸ discusses

instrumentation requirements in sugar boiling as visualized in Hawaii. Others who have discussed the general subject are DELDEN⁵⁹, VENTON⁶⁰, and COLE⁶¹.

HALL¹⁷ describes a particularly complete automatic control system for vacuum pans. A supersaturation recorder-controller is the basic element of

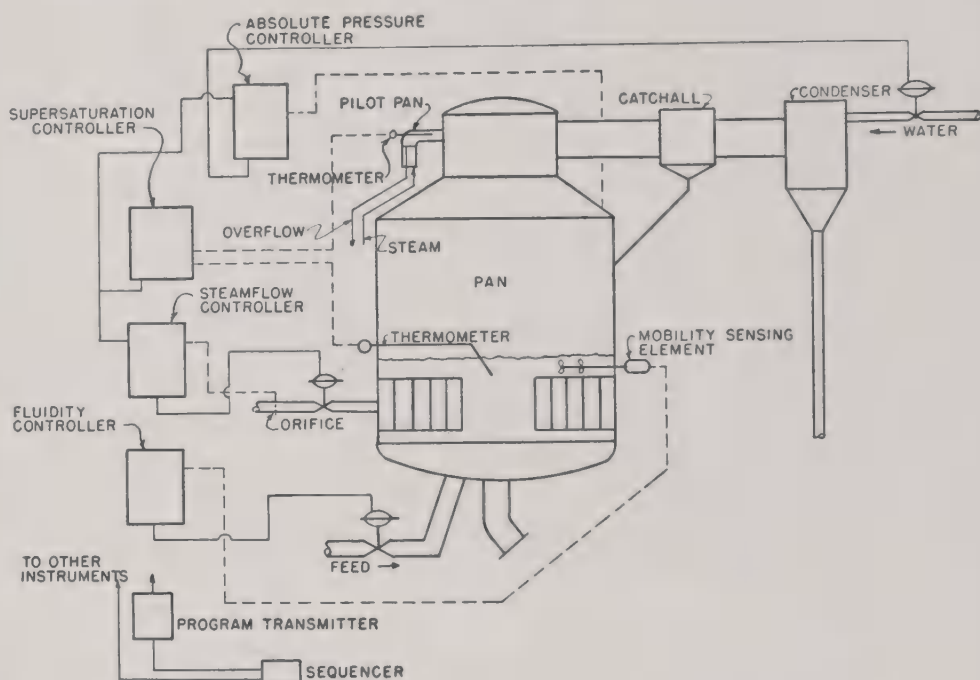


Fig. 6/12. System for automatic pan control – Minneapolis-Honeywell Regulator Company, BROWN Instrument Division.

four interacting control loops. Absolute pressure is controlled through a throttling butterfly valve which regulates water to the barometric condenser. The steam flow to the calandria is measured and pneumatically proportioned by means of a pneumatic flow controller. Mobility of massecuite is indicated by an agitator paddle. The power load on the paddle is used as a means of regulating pan feed. Supersaturation is used as a basis for controlling the seed point. A diagrammatic sketch of the arrangement is shown in Fig. 6/12.

The Fischer and Porter Company⁶² have marketed an indicating instrument for pan control. This is a combination instrument which gives an indication of supersaturation, absolute pressure, massecuite temperature, pan vapor temperature, and boiling point rise. All of these variables are obtained from two measurements, absolute pressure and massecuite temperature. Indications are by three pens. Conversions to supersaturation are obtained by use of charts which underlay the pens.

Fig. 6/13 shows a photograph of an instrument panel for a modern pan control system at the C and H refinery at Crockett. The instrument in the upper lefthand corner is an absolute pressure regulator with a cam arrangement for a predetermined time cycle as previously described. Associated with this is the mercury column absolute pressure gage in the left center.

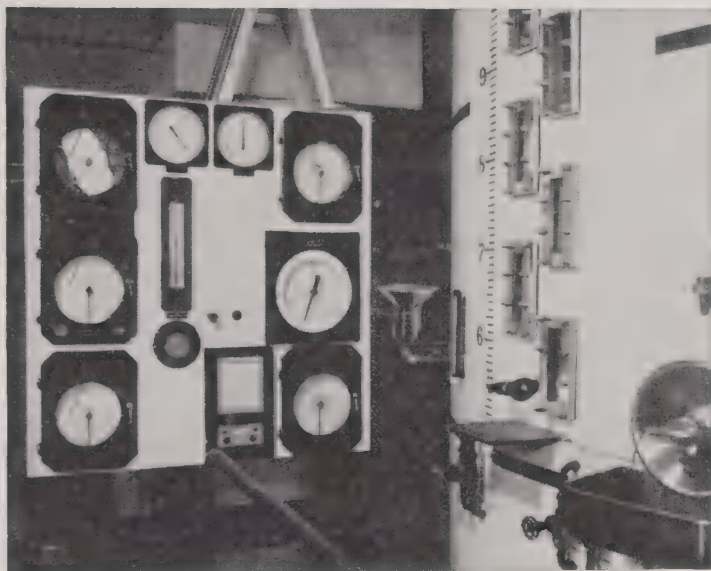


Fig. 6/13. Pan instrument panel – California and Hawaiian Sugar Refining Corporation.

The BROWN supersaturation recorder is shown in the right center near the seed cup. At the bottom center is the recording wattmeter on the stirrer motor for controlling feed to the pan. The other instruments indicate and record vacuum, temperature, level, steam pressure, steam flow, etc.

7. Summary

In summarizing, it is evident that a great deal of effort has been made to develop techniques, methods, and equipment for controlling crystallization processes in the sugar industry. This has required development of the most precise data possible on certain properties of sugar solutions and the utilization of these in development of accurate measuring instruments and reliable control equipment. Refineries today make most of these instruments available to the sugar boiler.

The controls generally provided include the following:

- (a) Automatic control of absolute pressure by controlling the flow of water to the pan condenser.

- (b) Automatic measurement of supersaturation for control of graining.
- (c) Automatic control of fluidity by regulating the feed to the pan.

Controls may also be provided to control steam flow to the coils or calandria, record massecuite level in the vacuum pan, etc.

Use of such equipment greatly assist the sugar boiler. When combined with good pan design and well developed techniques, a uniform size, high quality sugar can be consistently obtained.

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CHAPTER 7

APPLICATION OF THE CONDUCTIVITY METHOD TO CONTROL THE CRYSTALLIZATION PROCESS AND SEEDING TECHNIQUE

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1. Introduction

The practical application of the electrical conductivity determination of sugar solutions as a criterion for the crystallization phenomena was started as a laboratory study at the Experiment Station for the Java Sugar Industry in 1927. This study was based on the following considerations:

1. The crystallization of supersaturated sugar solutions has undoubtedly to do with the rate of diffusion, and the rate of diffusion is related to the viscosity.
2. It is a well known fact that the mobility of ions in solutions determining the electrical conductivity is directly related to the viscosity. This relationship was studied by WALDEN¹ in 1906, who stated that in solutions with the same electrolyte concentration, the relationship between the conductivity and the viscosity can be expressed by the equation:

$$\text{conductivity} \times \text{viscosity} = \text{constant}$$

3. The practical method used by sugar boilers to determine the degree of supersaturation of sugar solutions is based on a visual observation of the viscosity by the so-called string proof.

A number of studies were made on the differences in the conductivity of technical sugar solutions in relation to the viscosity with two objectives in mind:

- (a) To determine whether there existed fundamental differences in the specific conductance of electrolytes in technical sugar solutions of a known degree of saturation, respectively supersaturation as a result of the purification technique, respectively the presence of certain types of nonsugars.
- (b) To determine the relationship between the conductivity and the

viscosity of supersaturated sugar solutions and to find out the quantitative relationship with the intention to apply this relationship for the determination of the supersaturation.

The results of a number of these studies were published in the *Mededeelingen van het Proefstation voor de Java Suikerindustrie* by HONIG, CORVER and NICOLA under the title: ‘On the relation of viscosity, electrical conductivity and supersaturation’ as a practical approach to the application of the conductivity control method for the crystallization process. The history of these developments has been described in the *Mededeelingen* by HONIG and ALEWIJN in 1934².

Simultaneously, the application of the conductivity control method was studied and introduced in Germany, Czechoslovakia and other European countries based on the first publications of the Java Sugar Experiment Station. Independent of these studies in Java in 1931, COURRIÈRE introduced in the French sugar industry an instrument based on the same principle, which he has given the name of tarphomètre.

According to our knowledge on the development and the introduction of this instrument in the practical sugar industry, the first steps were made in the Java sugar industry. Approximately in the same period a similar system was introduced independently in the French sugar industry. The first systematic studies on the relationship between viscosity, supersaturation and conductivity of technical sugar solutions were made at the Experiment Station of the Java sugar industry.

This instrument called by the Java Experiment Station the ‘conductivity control instrument’ or ‘electrical apparatus for the control on the boiling process’ was given the name of ‘cuitometer’ by British manufacturers of

TABLE 1

Concentrated sugar solution in brix	Conductivity in reciprocal ohms
67.9	0.00446
73.9	0.00233
77.4	0.00168

this control equipment. This is the name under which it is best known in the English literature.

It is a well known fact that the conductivity of concentrated sugar solutions decreases with an increase of the concentration. In Table 1 we give the data to demonstrate this relationship.

The sugar concentration varies from 75 to 85 during the crystallization process. It is important for a well conducted and controlled crystallization that the brix of the mother liquor does not show a greater variation than 1° brix.

For the *A*-boilings in raw sugar mills at a temperature of 65° C and 80 brix, there is a considerable variation in the specific conductance of the different raw materials depending on the ash content and the ash composition. As extreme values, the specific conductance can vary from 0.0002 to 0.001 reciprocal ohms.

It was felt when this method was introduced that there had to be a correction adjusted to the specific conductance of the raw material to be crystallized. The simplest way to achieve this result was by using a variable voltage for the circuit of which the conductivity had to be measured. This is technically speaking the simplest solution to get a reproducible recording of the saturation values with an elimination of the variations in the ash content, respectively the specific conductance of the raw materials.

The practical experience has shown that the conductivity control method is an objective method to control the crystallization process. It has found its place in the sugar industry alongside the determination of the boiling point elevation to control the supersaturation and the determination of the brix via the refractive index.

2. The Use of the Cuitometer as Operational Control Instrument

(a) *The Judgment of the Pan Boiler*

The skill of the pan operator to determine the degree of supersaturation of crystallizing sugar solutions is based primarily on his ability to estimate and to judge the viscosity of crystallizing liquors via a string proof, determining the fluidity between index and thumb. It is difficult to translate this subjective appraisal of the consistency in exact terms; it is a visual determination of the viscosity combined with the intensity of feeling in touching sugar liquors. It has to be realized that if a pan sample is taken on a glass plate, it cools down immediately with a tremendous change in the viscosity. It is impossible to describe this operational control method as being exact; it is highly subjective. It has been found by checking the judgment of pan operators with proper control instruments as, for instance, the boiling point elevation or with pan refractometers that the opinion as to the tolerated degree of supersaturation based on a string proof varied at random.

(b) *Viscosity and Conductivity*

It is, however, true that viscosity is related to the concentration of sugar solutions. The more concentrated a sugar solution is, the higher the viscosity. It was in 1928 in studying the physical characteristics of technical sugar solutions, investigating the relationship between viscosity, respectively conductivity of sugar solutions primarily to find an objective way for the determination of deviations in the viscosity of low grade boilings, that one of us used the conductivity of concentrated sugar solutions as an indirect measure for the viscosity.

There are a number of opinions on the effect of modifications of processing on the viscosity of afterproduct boilings as, for instance, a high lime content in clarified juice results in a high viscosity of afterproducts and final molasses; processing of stale cane, respectively overmature cane results in a high viscosity of the third boilings; reprocessing of molasses is one of the main causes of high viscosity in third boilings, etc.

There are a number of practical rules, better to be qualified as prejudices which never have been proved actually but which are repeated over and over again as if it were well established facts. The intention of our investigation was to replace the viscosity determination, which is a time consuming analysis, by an uncomplicated simple method being the determination of the

TABLE 2

BRIX, SUPERSATURATION, VISCOSITY AND ELECTRICAL CONDUCTANCE OF SUCROSE SOLUTIONS CONTAINING 2% KCl % SUCROSE, AT 50° C

Brix	Super-saturation	Viscosity in poises	Cond. $\times 10^{-6}$	Resistance in $\Omega \times 10^3$	KCl conc. in g/100 ml	Corr. factor to be applied to 2g/100 ml	Conduct. corr. for equal KCl conc.
72	0.968	0.70	1842	0.543	1.962	1.019	1877
73	1.018	0.87	1479	0.676	1.998	1.001	1481
74	1.072	1.12	1277	0.783	2.034	0.983	1255
75	1.130	1.43	1117	0.895	2.072	0.965	1077
76	1.192	1.79	958	1.043	2.110	0.947	907
77	1.260	2.33	799	1.251	2.148	0.931	744
78	1.335	3.05	654	1.529	2.186	0.915	598

electrical conductivity. In physical chemistry there is a simple rule on the relationship between viscosity and electrical conductivity known under the name of the rule of WALDEN, stating that the product of viscosity and electrical conductivity for the same concentration of electrolyte per unit of volume is constant.

We have checked this rule, and it has been found that it is not exactly correct for concentrated sugar solutions. We find, for instance, for 2% KCl on refined sugar for different concentrations the values as given in Table 2.

(c) *Specific Conductance of Sugar Solutions*

The determination of the electrical conductivity of sugar solutions is simple and rapid. It is essential that in this determination the temperature of the sugar solution (respectively molasses) is kept at a constant temperature. The conductivity increases with the rise in temperature. Furthermore, it has to be determined with an alternating current. There is no objection to use the standard frequency of AC as used for sugar mills (50 or 60 per second).

It is customary to express the conductivity in reciprocal ohms or mho's for a cubic unit, being a volume with a cross-sectional area of 1 cm² at a distance of 1 cm (or with a length of the conducting medium). This is the specific conductance.

The resistance of any conducting medium is proportional to the distance of the electrodes, resp. the length of the conducting medium (L) and inversely proportional to the surface area of the electrodes, resp. the cross-sectional area between the electrodes (A); or with the specific resistance of the medium (r), the total resistance of any type of cell (or electrode set) mounted in a fixed position is:

$$R = r \frac{L}{A}$$

It has been the endeavor in the technical construction of technical cells or a set of electrodes (as they are commonly called in the conductivity control of the boiling process) to make the capacity $\frac{L}{A}$ for raw sugar factories equivalent to a capacity of one cubic unit:

$$\left(\frac{\text{distance between electrodes in cm} = L}{\text{cross-sectional area in cm}^2 = A} = 1 \right)$$

The conductance of the raw materials used in the boiling house in cane-sugar mills for crystallization from saturated syrup to supersaturated final molasses varies from 200 to 20,000 $\times 10^{-6}$ mho, or expressed as the specific resistance from 500 to 50,000 ohm per cubic unit.

(d) *Mathematical Relation of Viscosity and Conductance*

The relationship between the viscosity and the conductance of highly concentrated sugar solutions can be expressed by the formula:

$$\text{conductance} \times \text{viscosity}^n = C$$

The exponent n is smaller than 1.0.

In Fig. 7/1 we give an example of such a relationship, tabulated in Table 1.

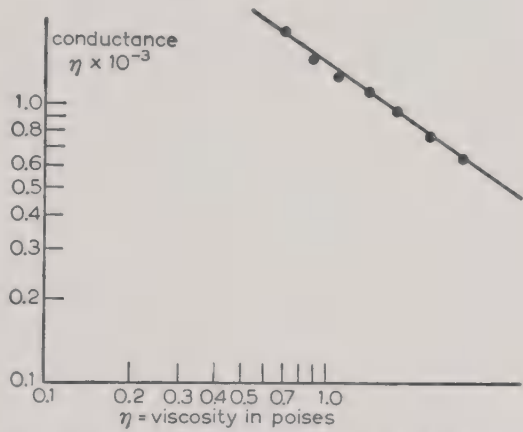


Fig. 7/1. Relation between viscosity and conductance of sucrose solutions, containing 2% KCl on sucrose at 50° C between 72 and 78 brix.

The relation can be expressed by the equation:

$$\log \text{cond. in mho's} \times 10^{-3} + 0.71 \log \text{visc. in poises} = C$$

or

$$\text{conductance} \times \text{viscosity}^{0.71} = C.$$

(The ordinates for viscosity and conductance are given in the logarithmic scale.)

The data used in this graph were determined accurately in the laboratory. It is valuable to determine the exact relationship between viscosity and

TABLE 3
CONDUCTANCE CORRECTED TO THE SAME KCl CONCENTRATION
(2.00 G/100 ML) BY THE FORMULA

$$\eta \text{ CORRECTED} = \eta \text{ AT BRIX } a \times \frac{2}{\text{KCl CONC. AT BRIX } a}$$

Brix	$\eta \text{ corr.} \times 10^{-6}$
72	1877
73	1481
74	1255
75	1077
76	907
77	744
78	598

electrical conductance to make the comparison for a uniform salt concentration per unit of volume. Using the data of Table 1 to calculate the conductance corrected for the same KCl-concentration, the low values are found as given in Table 3.

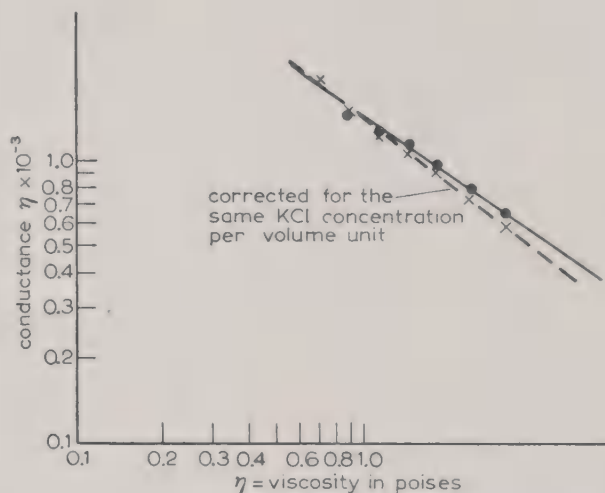


Fig. 7/2. Relation between viscosity and conductance of sucrose-KCl solution at 50° C can be given by the equation:

$$\log. \text{ cond. in mho's } \times 10^{-3} + 0.71 \log \text{ visc. in poises} = C$$

or

$$\text{conductance} \times \text{viscosity}^{0.71} = C.$$

Correcting the conductance for the same KCl concentration per unit of volume (2 g per 100 ml) the relation can be expressed by the equation:

$$\text{conductance} \times \text{viscosity}^{0.80} = c$$

(The ordinates for viscosity and conductance are given in the logarithmic scale.)

This relation between viscosity and corrected conductance has been represented in Fig. 7/2 together with the relationship between viscosity and conductance *uncorrected* for the salt concentration. Fundamentally, there is no change in this relationship. When the conductance is corrected for the same salt concentration per unit of volume, the exponent n approaches the value 1.0.

(e) *Supersaturation, Viscosity and Conductance*

A large number of determinations has been made to determine the relationship between supersaturation and viscosity, respectively the supersaturation and the conductance. In Fig. 7/3 we give an example of these determinations made with solutions of pure sucrose to which 2% KCl had been added. Of these solutions have been determined accurately the saturation values at different temperatures. It follows from these determinations that the ratio

of viscosity (or electrical resistance (1/cond.) of sugar solutions and super-saturation can be represented by a very simple formula:

supersaturation (or brix) = $n \cdot \log. \text{ viscosity}$

or

supersaturation (or brix) = $\eta \cdot \log. \text{ resistance}$

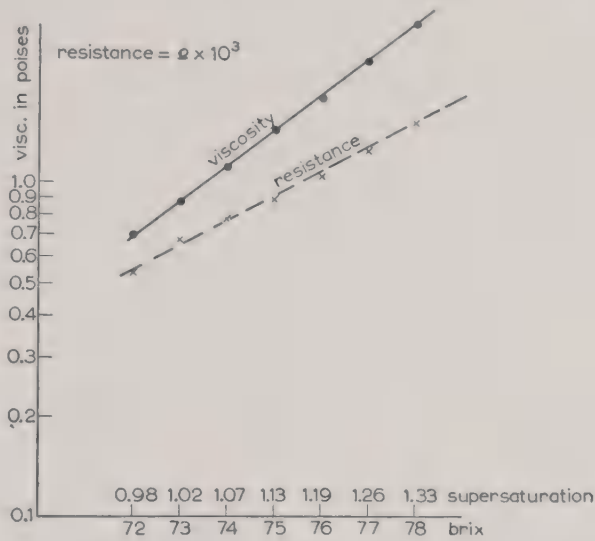


Fig. 7/3. Relation between brix (and supersaturation) of the sucrose-KCl solution (2% KCl on sucrose) and the viscosity and the resistance $\left(\frac{1}{\text{conductance}}\right)$ at 50° C.

Using linear coordinates for the conductance and the supersaturation, we

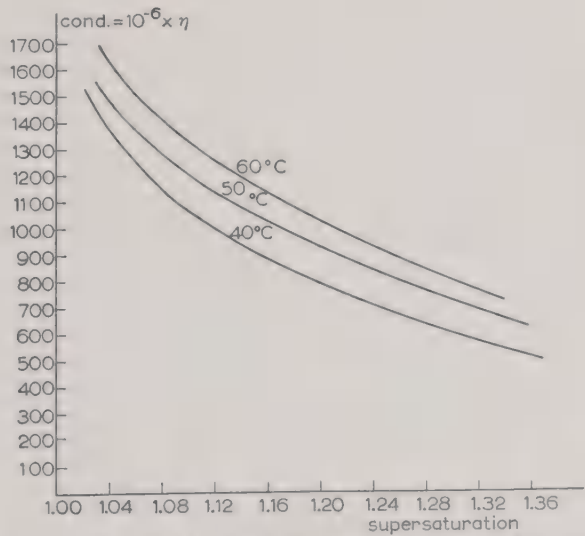


Fig. 7/4. Relation between the conductivity of a sucrose-KCl solution (2% KCl on sucrose) and supersaturation at 40°, 50° and 60° C.

find relationships as given in Fig. 7/4 for solutions of sucrose and KCl.

For molasses of low purity and at temperatures used in crystallizer operations, the relation between viscosity and electrical conductance has been determined in the same way. For two molasses having the following composition as received from the factories and obtained under normal operational conditions:

	sf. Ass.	sf. Gemp.
Brix	95.5	95.7
Pol	32.1	27.1
App. purity	33.6	28.3
Clerget sucrose	36.7	32.4
Sucrose purity	38.8	33.9
Reducing sugars	15.1	26.1
Uncorr. sulphated ash	18.85	13.0
True dry solids	82.0	84.0
True purity sucrose/true dry solids	44.8	38.6
RS/ash ratio	0.80	2.01

These molasses samples were diluted with water to free them from any trace of crystallized sucrose, reconstituted and diluted to different concentrations for the determination of viscosity and conductance. The values were as given in Tables 4a and 4b and are represented graphically in Fig. 7/5.

TABLE 4a
VISCOSITY AND CONDUCTANCE OF MOLASSES WITH HIGH ASH CONTENT³
TEMP. 50° C ASH 20.3%
C. ASSEMBAGUES

Brix	True dry solids	Viscosity in poises	Cond. $\times 10^{-6}$
96.2	82.7	45.7	912
95.0	81.7	28.6	1201
94.2	81.0	22.6	1451
93.9	80.7	19.5	1677
92.7	79.7	12.8	2122
92.0	79.1	10.5	2331
91.0	78.2	8.9	2987

(f) *Conductance and Technical Sugar Crystallization*

As a general rule, the reciprocal value of conductance or the electrical resistance of concentrated sugar solutions varies in the same way as the viscosity, and it is possible to use the conductance as an indication for the

concentration, respectively the supersaturation of crystallizing sugar solutions.

TABLE 4b
VISCOSITY AND CONDUCTANCE OF MOLASSES WITH LOW ASH CONTENT³
TEMP. 50° C ASH 12.9%
C. GEMPOLKREP

Brix	True dry solids	Viscosity in poises	Cond. × 10 ⁻⁶
95.2	86.0	77.8	203
93.6	84.6	40.2	284
92.9	84.0	27.7	374
91.1	82.3	17.2	527
90.1	81.4	15.5	646

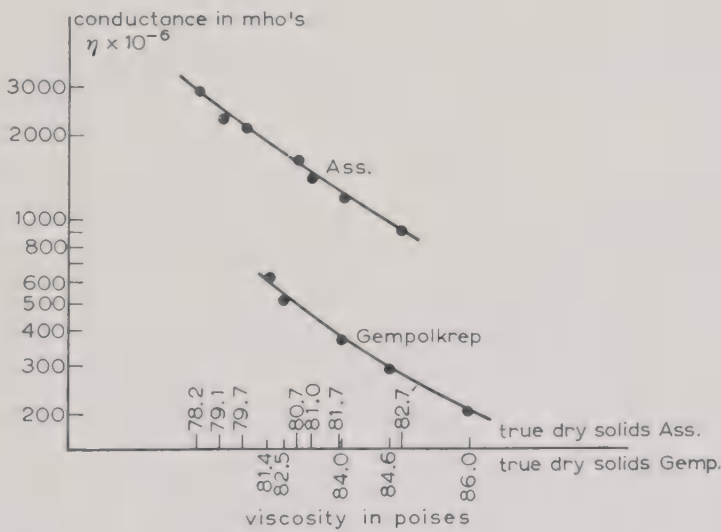


Fig. 7/5. Relationship between electrical conductivity and viscosity in poises at 50° C for 2 molasses with a high (Assembagoes, 20.3% ash on true solids) and a low (Gempolkrep, 12.9% ash on true solids) ash content.

This relation can be expressed by the usual formula:
 $\log \text{ cond.} + n \log \text{ visc.} = c$
or
 $\text{ cond.} \times \text{ visc.}^n = c$

It must be understood that the relationship between purity, supersaturation, temperature and conductance is complex. It is not possible with the available data to give a simple mathematical expression for the relationship between the variables entering into the operational conditions of practical and technical crystallization of sucrose. There are, however, in the normal

working conditions in sugar factories certain limitations in the variations in the most important operational criteria. For *A*-, *B*- and *C*-boilings in raw sugar mills, the purity of the three types of boilings varies normally as given in Table 5.

Another limitation in the practical application of the conductivity as a criterion for the concentration is the temperature of the crystallization process. The common practice is to use at present a crystallization technique applying for the different types of boiling a maximum vacuum of 25"-26" mercury or an absolute pressure of 0.06-0.08 kg/cm².

For the purities as given in Table 4, the boiling point elevation at the saturation point varies for this absolute pressure of 0.06 to 0.08 kg/cm² between 8° and 13° C. The normal boiling point elevations found in *A*, *B* and *C*-boilings for a vacuum range of 25"-26", with the corresponding fluctuations in the supersaturation, are also given in Table 5.

This boiling point elevation is the increase in temperature in boiling technical sugar solutions over the temperature of pure water. The boiling point for pure water is given for vacua from 25"-28" in Table 6. The normal working vacua for *A* and *B*-boilings are, as stated, in a modern well-

TABLE 5
THREE-BOILING SYSTEM OF CANESUGAR MILLS; VACUUM 25"-26"

	Purities	Brix at saturation	Temperatures in pans in °C	Boiling point elevation in °C	Max. supersaturation used in cryst. process in pans, excl. of nucleation	Max. boiling point resulting from applied supersaturation in °C
<i>A</i> -massecuite and syrup	82-88	76-78	61-65°	8- 9°	1.20	1.6-1.8
<i>B</i> -massecuite and <i>A</i> -molasses	70-76	78-79	63-67°	9-10°	1.30	2.7-2.8
<i>C</i> -massecuite and <i>B</i> -molasses	58-64	80-82	65-69°	10-11°	1.35	3.5-4.5
Final molasses at moment of discharging <i>C</i> -massecuite from pan	36-42	83-84	67-72°	11-13°	1.40	4.0-6.0

equipped factory 25"-26". It is preferable to have the best possible vacuum in the *C*-boilings for a minimum decomposition in this type of boiling. One inch difference in vacuum makes for the same supersaturation a difference in the boiling point of more than 6° to 7° C (or 11° to 12° F).

The practical problem of the application of the conductivity control is

reduced in this way to the problem to determine the fluctuations of the conductance for a certain range of purities and supersaturations, and to find out whether these variations in the conductance value give an applicable indication as such for the conditions of crystallization, respectively rate of

TABLE 6
BOILING POINT AND PRESSURE OF WATER UNDER THE CONDITIONS OF THE BOILING HOUSE
IN SUGAR MILLS

Vacuum in inches Hg	Vacuum in cm Hg	Absolute pressure		Temperature	
		in psi abs.	in kg/cm ²	°F	°C
28	71.1	0.94	0.032	100.05°	37.8°
27	68.6	1.44	0.050	114.3°	45.7°
26	66.0	1.93	0.067	124.9°	51.6°
25	63.5	2.43	0.084	133.3°	56.3°

crystallization, formation of new nuclei and dissolving of crystallized sucrose as a result of the state of saturation.

The answer to this question is that this can be done and that the use of the determined conductivity is a much better guide than the use of the viscosity that is estimated by a string proof.

What are the normal fluctuations in the conductance of the different types of boiling? These variations are determined primarily by the variations in the purity combined with variations in the ash content of the nonsugars. It are primarily the ash constituents which are the determining elements for the conductivity. Furthermore is important the vacuum on the pans. An optimum vacuum results for the same degree of supersaturation in a lower temperature of the massecuite. This corresponds with a lower conductance. This is more or less an element in the conductance control determined by the technical efficiency of the installed factory equipment.

The ash content, determining primarily the conductance of technical sugar solutions at constant temperature and brix, varies from mill to mill, but as a rule the daily variations are in raw sugar mills determined by the purity of the considered sugar house products. We are using as the normal expression for the ash content, ash % nonsugars, being characteristic for a certain area and period of harvesting. For molasses of Cuban mills the value

$$\frac{\text{ash}}{\text{brix} - \text{pol}} \times 100$$
 varies between 15 and 20. For the three-boiling systems the ash content of the boilings (and syrup and molasses*) varies as given in Table 7.

* Calculated by the formula: $\text{brix} \frac{100 - \text{purity}}{100} \times 0.15$ to 0.20

TABLE 7

	Purities	Brix at saturation	Ash content % massecuite at saturation concentration*
A-massecuite and syrup	82-88	76-78	1.4- 2.8
B-massecuite and A-molasses	70-76	78-80	2.8- 4.7
C-massecuite and B-molasses	58-64	80-82	5.2- 5.8
final molasses	36-42	83-85	7.3-10.7

For a syrup in canesugar mills of a purity 80 at a temperature of 65° C, the solubility of sucrose at saturation is 3.05 % water. The brix of this solution is 79.2.

An increase of 0.5 in brix corresponds with an increase in the supersaturation** of $\frac{79.7 \times 0.80}{3.05} = \frac{100 - 79.7}{3.05} = \frac{3.12}{3.05} = 1.03$. This gives a decrease in the electrical conductance of approximately 7 to 8 %.

In the concentration range of the crystallization process, a change of 0.1 brix of the sugar solution gives at constant temperature a change in the electrical conductance of 1 to 1.5 %. A change in the supersaturation from 1.10 to 1.30 reduces the conductance to approximately 50 % of the conductance at 1.10 supersaturation.

It can be agreed that the conductivity control is only reliable for identical operational conditions for boilings of the same purity and nonsugar composition.

But the same arguments exist for other control systems; boiling point elevation and pan refractometer control have also to make their compensations for vacuum level and vacuum fluctuations.

(g) *Electrode Cells in Technical Conductivity Control*

What kind of electrodes must be used for technical boiling house control?

The development of the construction and design of electrodes shows different aspects. The endeavor was from the beginning to construct the electrode cell with a capacity equal to 1 cubic unit (distance and cross-section

* Calculated by the formula: $\text{brix} \frac{100 - \text{purity}}{100} \times 0.15 \text{ to } 0.20$.
** The supersaturation has been calculated in the classical way as:
 $\text{supersaturation} = \frac{\text{sucrose present per 100 water at temp. T}}{\text{sucrose dissolved in a saturated sugar solution of the same purity at temp. T}}$

= 1). It had to be installed in the pan in such a way that the crystallizing fill mass was flowing freely between the electrodes, that the measured conductivity could be considered to be representative of the circulating fill mass. This was achieved by using small metal cylinders as electrodes. In mounting these electrodes in the pan wall, the position of the electrode was independent

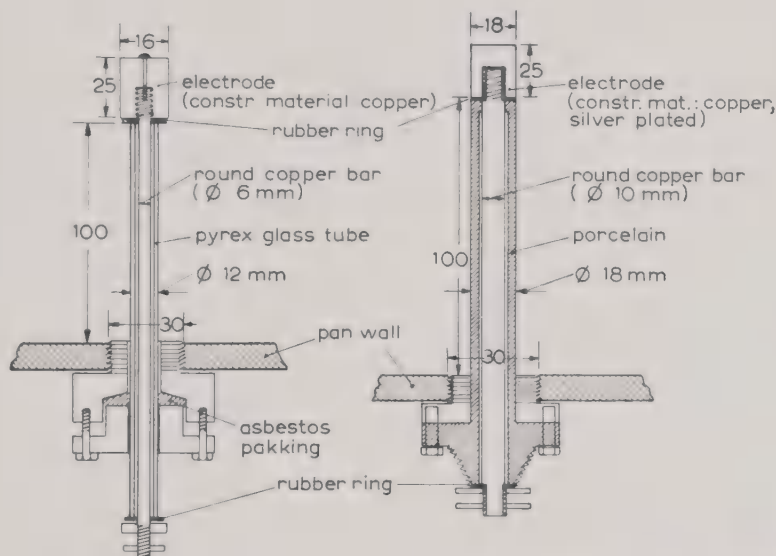


Fig. 7/6. Construction of the first type of electrode as used in the Java sugar industry in 1931. As insulation material was used glass. The electrode was supported by a copper rod of 6 mm diameter. This type of electrode was occasionally damaged, particularly in discharging pans where the glass insulation broke near the pan wall.

Fig. 7/7. Electrode introduced in 1932. Insulation: porcelain. The electrode itself has been silver plated to reduce the formation of scale affecting the capacity of the electrode set. The copper conductor supporting the electrode has been strengthened using a larger diameter for this supporting conductor (10 mm diameter).

of the system of mounting. The electrodes were placed in such a way that the axis between the electrodes, being the direction of the flow of the electrical current, was perpendicular to the flow of the crystallizing fill mass. Furthermore, it was necessary that the electrodes were installed insulated in the fill mass, far enough removed from metal surfaces either pan wall or the construction materials of supports and evaporating surfaces to be certain that what was measured actually was the conductivity of the crystallizing sugar product.

In the Figs. 7/6–7/11 we give schematic drawings of the development of the construction of the electrodes (resp. the construction of the electrode cell). In this construction, form of electrodes, absolute distances of electrodes and the flow of circulating fill mass of which the conductance has to be determined between the electrodes must be considered.

In recent years, electrodes have been constructed as a round metal cylinder mounted in a piece of modern insulating plastic of low conductivity, good

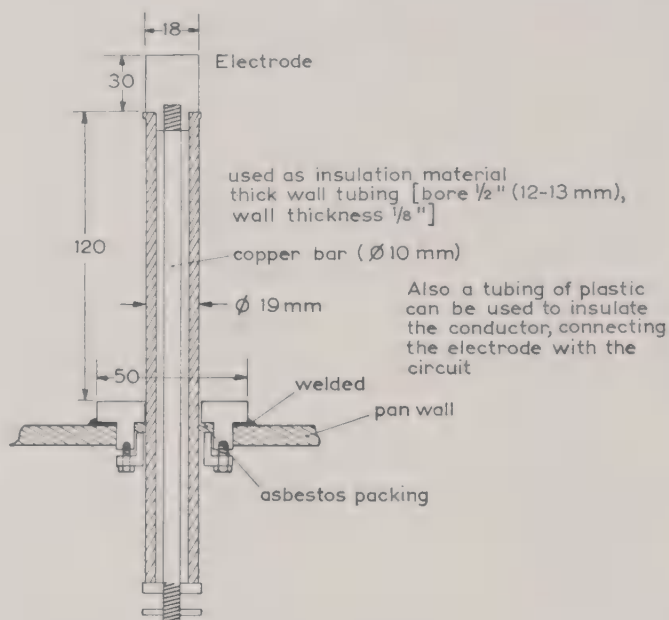


Fig. 7/8. Type of electrode made with rubber or plastic tubing as insulation. The gland to mount the electrode in the pan wall has been welded to the inside of the pan wall.

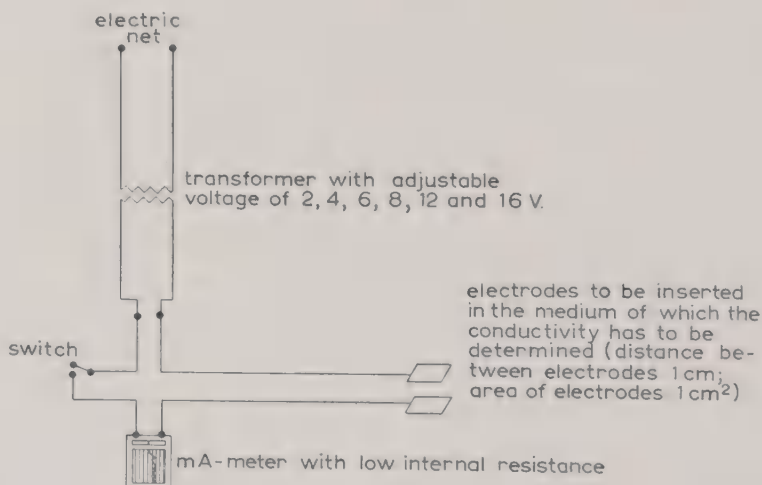


Fig. 7/9. Circuit for the determination of the conductivity of masscuits.

workability and of sufficient mechanical strength that it cannot be deformed or easily damaged as the result of the moving fill mass or as the result of the temperature fluctuations to which the electrode sets are subjected in steaming or filling the pans with syrup at the start of the boiling process. The plastics

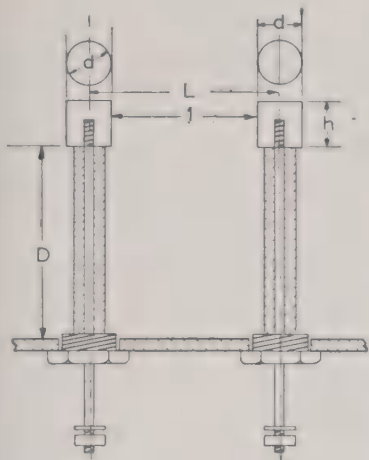


Fig. 7/10. In the mounting of technical electrodes in pans it is desirable that the following relation between the different essential dimensions is maintained:

$$\frac{L - \frac{1}{3}d}{h \times d} = 1 \text{ where } L = \text{distance between electrodes}$$

heart to heart, h = height of electrode, d = diameter of electrode. All dimensions have to be expressed in the same units, f.i. cm. In practice the following dimensions are used: $L = 5 - 8$, $h = 2\frac{1}{2} - 3$, $d = 1.6 - 2$. It is necessary that the distance of the electrodes to the pan wall is $D = 2L = 10 - 16$.

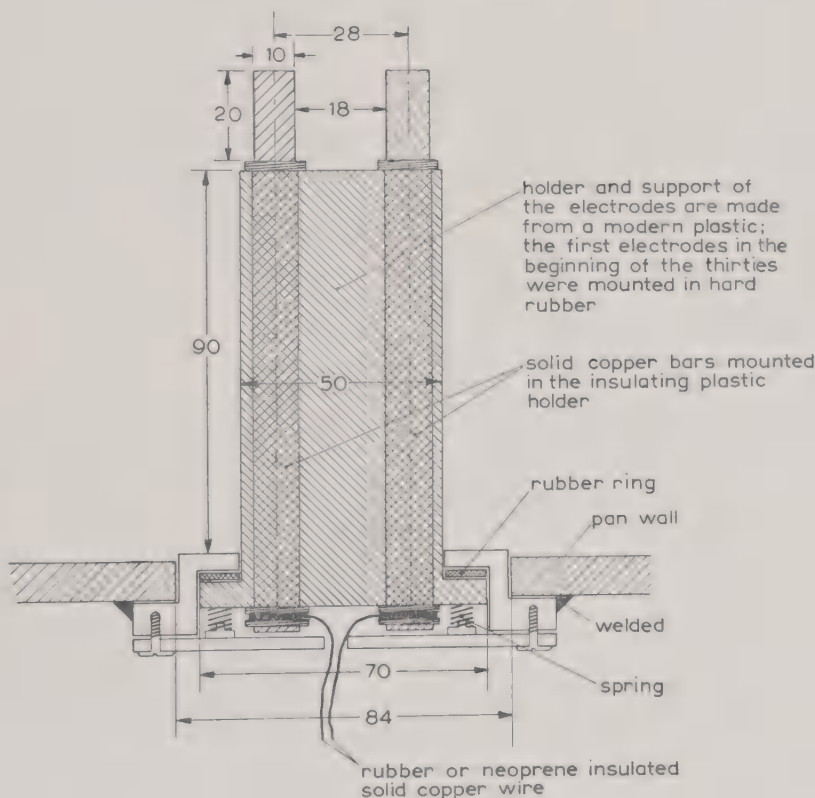


Fig. 7/11. To overcome the difficulties in mounting electrodes in pans to have equal capacities for the electrode cells in different pans, electrodes have been developed where both electrodes are inserted in one rigid supporting holder. It is possible to calibrate these electrode cells and to make the capacity exactly equal to 1 cubic unit (cm^3). With modern plastics which can be obtained as molding materials it is possible to construct these electrodes in the workshops of the sugar factories. A number of these modern plastics have a good workability and can easily be finished at the exact dimensions as required for inserting the electrodes and to have a set of electrodes of a predetermined capacity with an accuracy of $\pm 2\%$.

that can be used for this purpose are numerous. Some can be obtained as powder or liquid molding material, and it is possible that the electrodes are constructed by the sugar mills themselves.

The endeavor has been to make electrode sets identically as to capacity, determined by the surface area and form of the electrodes and the relative distance of the two electrodes. This makes it possible that in factories, for instance, one recording instrument can be used for recording either the conductivity at different places in the same pan or recording simultaneously the conductivity in different pans.

The calibration of the electrodes must be done in the laboratory with standard KCl-solutions and the proper kind of equipment for accurate conductance or resistance determinations. It is possible in many cases, if the capacity of the manufactured set of electrodes is not exactly one cubic unit, by reducing or increasing the surface area of the electrodes, to make the capacity exactly equal to the unit.

(h) *Magnitude of Conductance in Technical Raw Sugar Crystallization*

Considering the tables for the conductivity as met in actual practice, we have, with an electrode set of 1 cubic unit capacity, found that the electrical current for different voltages going through the crystallizing raw material is as follows (Table 8).

TABLE 8

Voltage AC 60 cycles/sec	Current in mA (scale range 0-100 mA)			Corresponding conductance in mho's $\eta \times 10^{-6} \times b$			Corresponding resistance in ohms $\Omega \times a$		
2	10	50	90	5000	25000	45450	200	40	22
4	10	50	90	2500	12500	22700	400	80	44
6	10	50	90	1667	8335	14925	600	120	67
8	10	50	90	1250	6250	11350	800	160	88
12	10	50	90	834	4167	8000	1200	240	125
16	10	50	90	625	3125	5650	1600	320	177
32	10	50	90	312	1560	2820	3200	640	355

It is for this reason that the technical equipment for conductivity control consists of a transformer of which an adjustable variable but constant voltage can be taken to such an extent that for the practical conditions of crystallization, the current fluctuates between 10-90 mA. This is fundamental in the construction of the equipment for the conductivity control.

The complete equipment consists of the following elements:

1. The electrodes, kept in a fixed position in the massecuite.
2. The source of the electric current, being alternating current of low

voltage. This voltage must be constant and must be adjustable to obtain a sufficient current that can be measured with standard control instruments. The voltage with the commercial conductivity control instruments can be varied and set at 2–32 volts. It is possible to use a variable transformer with a continuous voltage range as, for instance, Varitran made by Fisher Scientific Co. with a voltage range from 0–120, using as supply source the 110 V. 60 cycle line. Preferable for factory control is a transformer with fixed position for the standard voltages to be used in the conductivity determination.

3. The electric current going through the massecuite, determined by the conductivity of the massecuite, is indicated by an mA-meter or it can be registered by a recording mA instrument.

(i) *Commercial Conductivity Control Equipment*

The elements of the conductivity control system are generally available commercial electrical instruments:

1. A transformer with an adjustable voltage outlet.
2. An indicating or recording mA-meter with a low internal resistance.
3. Electrodes which can be constructed by the workshops of the sugar factory.

These elements can be ordered separately by the sugar mills and the electrodes are made in the workshop of the mill and then it is all assembled. It is a simple technical construction; the calibration can be done by the mill laboratory. It is also possible that the whole equipment is ordered from manufacturers specialized in control instruments. Well known manufacturers of conductivity control equipment are:

The Sugar Manufacturer's Supply Co., 7 & 8 Idol Lane, London E.C. 3, England, manufacturing the cuitometer;

HEEMAF, Hengelo, the Netherlands, manufacturing the electrical conductivity control meter;

George Kent, Ltd., 199–201 High Holborn, London W.C. 1, England, manufacturing conductivity instruments for boiling house control;

Ludwig Seibold, Helferstorferstrasse 6, Wien 1, Austria, manufacturing the 'Leitfähigkeit Kochkontroll Apparat';

S.E.C.I.P., (Promesur), 23 Rue Clapeyron, Paris 8^e, France, manufacturing the tarphomètre.

(j) *Application of Conductivity Control in Different Countries*

The total number of conductivity control instruments in use today over the whole world is estimated as follows:

Java, where this control method in the cane sugar industry originated	250
India and Formosa (Taiwan)	150
Australia	50
Mauritius and South Africa	30
European beetsugar industry, including Russia, Czechoslovakia, Poland and Hungary	400
European refineries	15
Western Hemisphere (U.S.A., Middle and South America, incl. Caribbean)	70
Philippines	15

It is surprising that the application of this method has found its broadest field in Java and neighboring countries, and in the European beetsugar industry. In Europe it is the result of the extensive studies made on this control system by the sugar research experiment stations in Berlin, Prague and Brno. Systematic studies made of this control method in the Western Hemisphere, including the Caribbean, are practically nihil.

The explanation may be that already other systems of pan control existed and were developed particularly in Hawaii and by the Crockett Refinery, and that the instruments required for control using the boiling point elevation had been developed to a great perfection by well known manufacturers of control equipment whose instruments had already found a wide application in the sugar industry in the Western Hemisphere.

A proof of the reliability of the conductivity control is that this method can be used for complete automatization of the crystallization process. In Australia and in the European beetsugar industry, pans have been equipped with recording instruments for measuring the conductivity which are operating simultaneously the intake valves for the pans, making it possible that from the time of the formation of the grain, respectively from the end of the built up of the footing the boiling process is done fully automatically and without human interference in the whole operation.

Equipment for the automatization of the boiling process using the conductivity values is constructed by:

George Kent, Ltd., 199-201 High Holborn, London W.C. 1, England;
Ludwig Seibold, Helferstorferstrasse 6, Wien 1, Austria.

(k) *Application of Conductivity Determinations on the Pan Floor*

In the technical application of the conductivity control, it is customary to apply a number of simplifications in the used equipment and in the interpretation of the measured conductivity.

It is possible that recorded mA readings are calibrated directly in supersaturation values. Equipment realizing this aim has been made and practically used. This equipment is based on the following relations:

(i) The specific conductance of any kind of raw material for the crystallization process from syrup to exhausted molasses, determined at 30° C and at a brix of 27 – 29, is 6.4 times the specific conductance of the same raw material at the saturation point at temperatures as normally met in pan work (65°–75° C).

This relationship can be used by constructing a set of test electrodes with a capacity exactly $\frac{1}{6.4}$ or 0.156 times the capacity of the technical electrodes inserted in the pan for practical control purposes.

By analyzing any kind of raw material with test electrodes on conductivity at 30° C and 27–29 brix, it is possible by adjusting the voltage of the transformer feeding the circuit to set the reading exactly at the saturation line. An example of such a setting is given in Fig. 7/12.

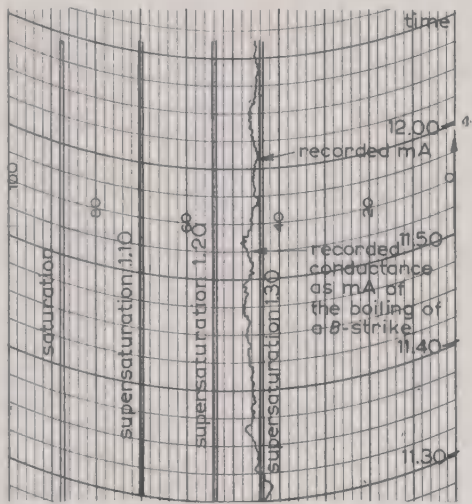


Fig. 7/12. Example of recording paper for conductivity control on which the saturation and supersaturation values are indicated. This system of recording is only possible by analyzing the raw materials for crystallization on specific conductance at 30° C and 27–29 brix with an electrode cell having a capacity of exactly 0.156 times the capacity of the pan electrodes. The zero line for this supersaturation control has to be set by adjustment of the transformer voltage according to the specific conductance of the tested raw material.

The normal materials for the crystallization process in canesugar mills with purities between 85 and 60 show the following relation between conductance (or mA meter readings) and supersaturation at temperatures between 65° and 70° C:

mA	supersaturation
88	1.00
70	1.10
54	1.20
44	1.30

Fig. 7/13. Graining of a footing for *C*-boilings with powdered sugar, suspended in alcohol, in *A*-molasses (purity 70–71, voltage transformer 12). Factory B. Pan boiler P.S.

Time	Reading mA-meter	Resistance of mc. in $\Omega \times a$	Cond. $n \times 10^{-6}$ $\times b$
9.05 Introduction of powdered sugar slurry, steam inlet on pan reduced (A)	28	428	2336
9.08 Started with continuous intake of movement water (B)	24	500	2000
9.25 End of use of movement water, grain well formed, steam inlet opened, started feeding pan with <i>B</i> -molasses (C)	50	240	4170

The feeding of the pan was regulated on mA-meter readings; it has been tried to maintain the mA-meter at 50 mA, it fluctuated actually between 39 and 56. This variation is considerable and corresponds with a variation in the supersaturation of at least 0.10.

Fig. 7/14. Graining of a footing for *C*-boilings with dry powdered sugar in *A*-molasses (purity 74–75, voltage transformer 12). Factory A. Pan boiler A.D.

Time	Reading mA-meter	Resistance of mc. in $\Omega \times a$	Cond. $n \times 10^{-6}$ $\times b$
9.12 Introduction of powdered sugar, started feeding pan with movement water and reducing steam inlet to pan (A)	24	500	2000
9.16 Increased the amount of movement water (B)	32	375	2666
9.25 End of use of movement water. Grain is well formed. The molasses has practically reached the saturation point (C)	77	156	6410
Started feeding pan with <i>A</i> -molasses. Steam inlet to pan full open			
9.40 Feeding of pan with <i>A</i> -molasses increased (D)	32	375	2666
9.40–12.10 conductivity maintained between 34 and 54 mA.			
11.50 started reducing feeding of pan, increasing slowly the concentration of the masse-cuite.			

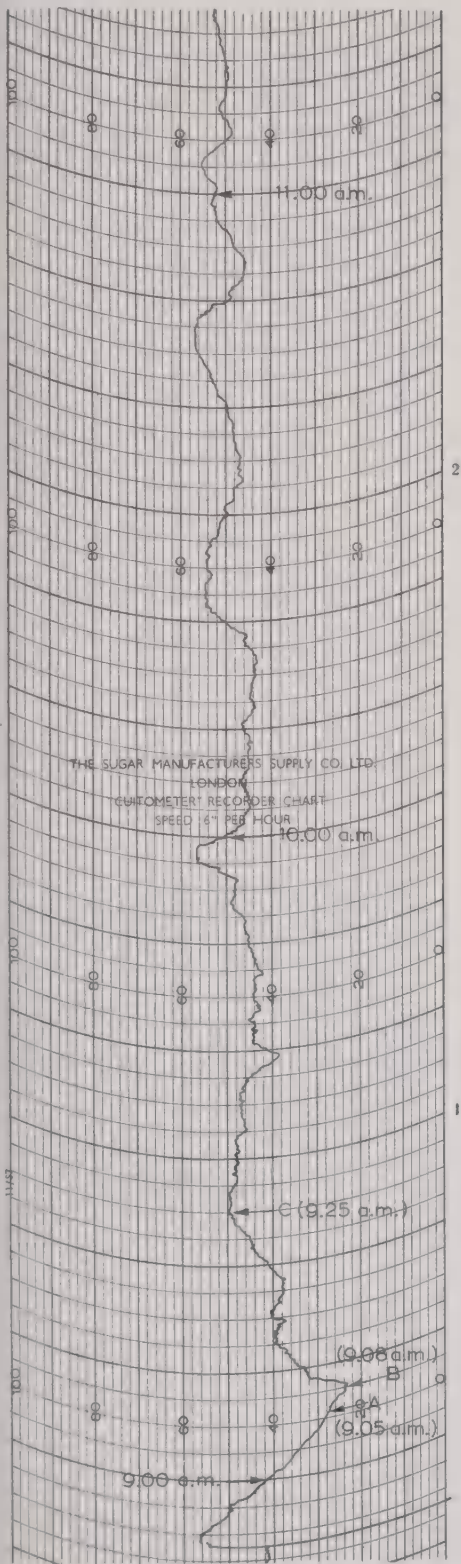


Fig. 7/13

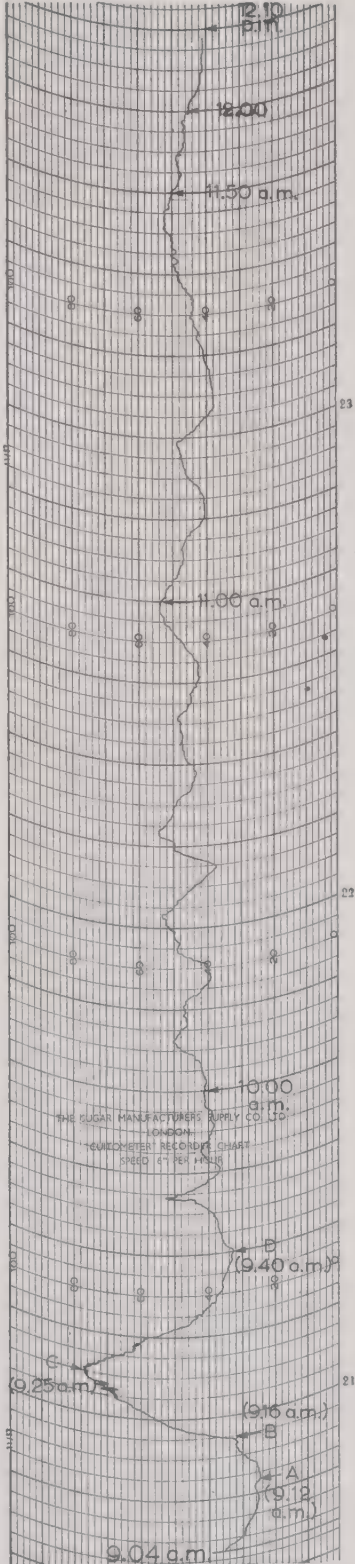


Fig. 7/14

Fig. 7/15. Recording of *B*-boiling started on a footing of *C*-sugar in syrup magma. The recorded graph is an example of an irregular form of boiling. The conductivity as indicated by the mA-meter readings fluctuated from 34–53. Voltage transformer 16. Temp. massecuite 68–69° C. Purity 74–75. At A a beginning of false grain formation could be observed. The secondary grain was not removed by washing. To dissolve secondary grain it is necessary that the massecuite is diluted below the saturation point, corresponding for this type of massecuite with approximately 65 mA-meter reading. The conditions of crystallization were as follows:

	mA-meter readings	
	34	53
Conductance $n \times 10^{-6} \times b$	2123	3311
Resistance in $\Omega \times a$	471	302

The lowest conductance corresponded with a supersaturation of approximately 1.30–1.35. The highest conductance corresponded with a supersaturation of approximately 1.15. This graph is an example of irregular feeding of the pan, a rather ‘stiff’ boiling.

Fig. 7/16. Recording of *B*-boiling started on a footing consisting of *C*-sugar and syrup. The recorded graph is an example of a well conducted boiling of *L*-massecuite. Voltage transformer 12. Temp. massecuite 70–71° C. Purity 72.

Sucrose solubility at circa 7–71° C and 72 purity = 358% water. The position of the inlet valve for *A*-molasses has been changed at the points A–G indicated in the recorded graph. The endeavor was to maintain the conductivity at a mA reading of 45. The actual fluctuation in the mA reading was from 39–52, corresponding with the following values:

	mA-meter readings	
	39	52
Conductance $n \times 10^{-6} \times b$	3247	4329
Resistance in $\Omega \times a$	308	231
Brix	85.9	83.4
Sucrose % water	4.39	3.61
$\left(\frac{\text{pol}}{100 - \text{brix}} \right)$		
Supersaturation	1.23	1.01

Characteristic for this system of boiling is that in the period from B — C the mass has been boiled in a ‘thin’ condition. At the point C the boiling has been stiffened but the character of the boiling remains fairly fluid.

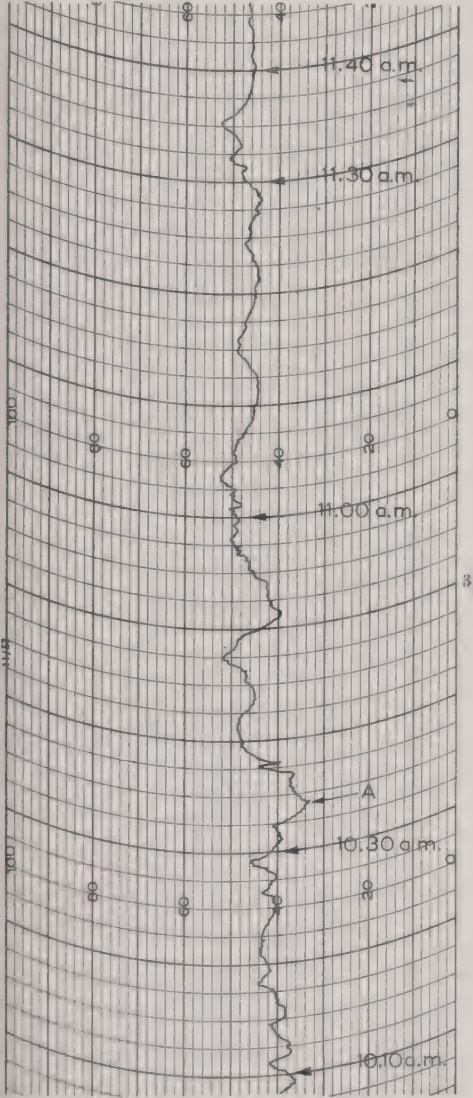


Fig. 7/15

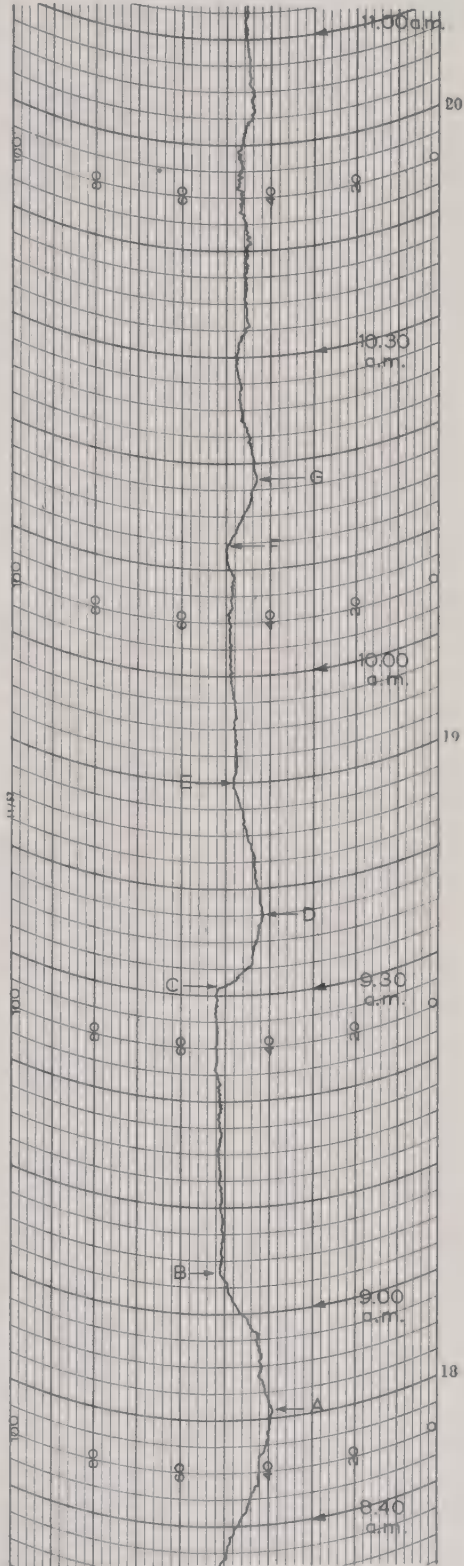


Fig. 7/16

The transformer voltage must be adjusted to a current of 88 mA when measuring the considered raw material with the test electrode at 30° C and 27–29 brix.

For the application of conductivity control, it is a most valuable relation when heating under stirring a saturated technical sugar solution (syrup or molasses) in which sucrose crystals have been suspended, although a certain amount of sucrose will dissolve resulting in an increase of the brix of the solution, that at the same time the effect of the rise in temperature on the conductance is counteracted and compensated by this increase in brix. Such a mixture *in the same state of saturation* shows small fluctuations in conductance with temperature variations. This is one of the great advantages of the conductivity control.

(ii) Under normal conditions we use the conductivity control primarily to apply the best technique developed at a certain mill by the best qualified and most experienced pan boiler as an example for the other boilers to follow. It is possible to make master charts for the different types of boiling as normally made. These master charts are used as an example of good operations for the other boilers who have less experience. It is also possible that a master chart after some time is developed by the factory staff, if they are familiar with the performance of different pans and normal raw materials.

A disadvantage is that we do not know in most cases the capacity of the electrodes that have been installed in the pans. Neither has it been customary up till now in most factories to apply the principle of test electrodes and to make special graph paper on which is given directly the supersaturation in relation to the conductance. This system can only be applied if we have electrodes of a known capacity; and it is necessary to make a special investigation on the characteristics of the whole control equipment. It is recommendable in this case to use a transformer with an accurately adjustable voltage.

(1) *Recorded Conductivity Charts of Boilings in Canesugar Mills*

In Figs. 7/13 and 7/14 we give two examples of the boiling of the footing for *C*-massecuites, using *A*-molasses as the material in which the grain has been formed via the introduction of powdered sugar. These two examples demonstrate that the technique of boiling at the two mills was not identical.

Although in both mills the seeding system of *A*-molasses with powdered sugar was relatively new (it had been introduced in 1954), it shows that in each of the mills a boiling system was developed with its own characteristics. The conductivity control is in this case a good illustration of the informative character of the conductivity registration. It teaches us the operation method

of the pan personnel and it enables us to analyze the operational conditions from which it can be stated whether fundamental misjudgments have been made by the pan operator.

In Figs. 7/15 and 7/16 we give two examples of a boiling of *B*-massecuite using the magma of *C*-sugar as footing. It demonstrates the different techniques of different pan boilers. One is using a regular intake with rather thin

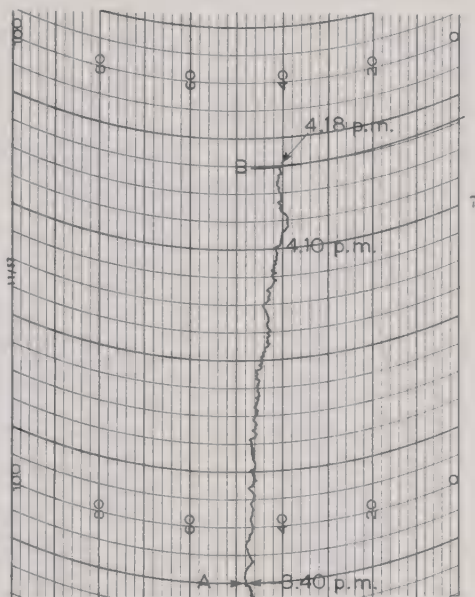


Fig. 7/17. Finishing *C*-boiling before discharging to crystallizers (purity 58.5, temp. massecuite 73–74° C, voltage transformer 32).

Time	Reading mA-meter	Resistance of mc. in $\Omega \times a$	Cond. $n \times 10^{-6}$ $\times b$
3.40 Stop of feeding <i>B</i> -molasses, continued boiling with the feeding of a small quantity of movement water to support circulation (A)	48	667	1500
4.18 End of boiling and pan discharge (B)	40	800	1250

This recorded graph is an example of the final phase of the boiling of *C*-massecuites to bring the concentration of the massecuite to be discharged to a high density, maintaining a good circulation by having a satisfactory rate of evaporation via the introduction of movement water.

boiling. The boiler whose work is represented by Fig. 7/15 is using as average a higher density but at the same time keeps the fluidity of the boiling much more irregular.

In Fig. 7/17 we give an example of the end of the *C*-boiling before discharging. This is an example of a typical and extremely valuable application

of the conductivity control. It is possible to end the *C*-strike before discharging at an exactly predetermined density, making it possible only by cooling in the crystallizers to be followed by reheating before centrifugation to get a maximum practical exhaustion of the final molasses, without application of any dilution water in the crystallizers.

Carefully analyzed experience has proved that at last the same purity of molasses can be obtained without any dilution of the massecuite in crystallizers if the *C*-massecuite is boiled to a known density in the pan before discharging.

A common mistake in boiling *C*-massecuites is that in the last hour of the strike before discharging, the density is brought to a too high level with the danger of overheating the massecuite in the pan as a result of insufficient circulation, and that the density is such that we are forced to dilute in the crystallizers to prevent breaking and damaging of the crystallizer equipment.

The only method we have at present to determine exactly the density of *C*-massecuites, respectively the viscosity in exact terms at the end of the strike, is by the application of the conductivity control system. Even if this application were the only conductivity control it had already deserved a prominent place among the modern control methods in sugar factories.

(m) *Modification of the Conductivity Control Method*

DUCASSE in Natal has introduced a control system based on the conductivity of the materials to be subjected to the crystallization process in pans, applying the voltage differential between two different metals as the source to have a small electric current to be measured passing between the electrodes.

It is possible with this system to have one isolated electrode in the massecuite and to use the pan wall as the other electrode. As the isolated electrode in the massecuite a zinc electrode can be used. The pan wall consisting of iron gives a potential difference of 0.25 to 0.8 V. The current is a direct current and can be measured with a sensitive micrometer. It is also possible to measure the voltage between electrode and pan wall as an indicator for the concentration of the massecuite. The set up of this control system is as given in Table 9.

The use of two different metals as electrodes in a crystallizing sugar solution produces a measurable direct current in the circuit which is determined by the voltage difference between the electrodes and the resistance between the electrodes. This system has been described in the literature and has been applied in a few Natal sugar factories⁴.

In Table 9 we give the differences between the two methods.

TABLE 9

	HONIG-ALEWIJN conductivity control	DUCASSE method
Electrodes	Cu, Ag or stainless steel; identical	Cu and Zn, or Cu and Fe; different
Voltage	4, 6, 8 or 16 V for control purposes, voltage constant	using the potential difference between the two electrodes; max. voltage diff. 1.10 V, voltage variable
Capacity of electrodes system	projected surface per electrode 6 cm ² ; distance 3 to 5 cm; cap. $\frac{1}{q}$ = 1 to 2; cap. of electrode system has preferably to be calibrated	Cu electrode flat; Zn electrode number of plates; cap. ext. ± 2 to 3
Type of current	alternating; 50 or 60 period/sec.	direct current
Type of control instrument	mA meter	micro V meter or micro A meter
Normal resistance for boiling process C-boilings	100–2000 Ω per cm ³	100–2000 Ω per cm ³
Current to be measured	0–100 mA	0–10 mA

3. Graining of Low Grade Boilings in Raw Sugar Mills

(a) *Graining of Low Grade Boilings with Powdered Sugar*

The graining technique for low grade boilings in canesugar factories becomes more and more a standardized operation, having the following characteristic elements:

1. The grain formation is done by seeding a supersaturated material in the vacuum pan with extremely fine powdered sugar introduced in the form of a slurry in an organic solvent having a low solubility for sucrose, or as a suspension of finely powdered sugars in a slightly supersaturated sugar liquor.

2. This seed grain is introduced in a supersaturated molasses of rather low purity, preferably an apparent purity between 70 and 75.

The advantage of a low purity of the footing is that the formed crystals are of great uniformity. There are practically no conglomerates. Occasionally there is the formation of twin crystals but this is primarily the result of the nonsugar composition and not of a controllable operational factor.

A disadvantage of the use of low grade molasses for graining is that it takes some time (15–35 minutes) before the small introduced nuclei have developed into well-formed crystals of a visible size which must be approxi-

TABLE 10 *
FULL SEEDING TECHNIQUES FOR *C*-MASSECUITES

Type of sugar used for seeding	Quantity used for low grade boilings	Purity of molasses used for grading	Calculated linear size of seed crystal
Confectioners 10X (DOMINO, Amer. Sugar Ref. Co.) used as dry sugar	$\frac{1}{2}$ -5 lbs./1000 cub. ft. of final <i>C</i> -massecuite	—	—
Confectioners 6X (JACK FROST, Nat. Sugar Ref. Co.) used as slurry in alcohol	2-5 lbs./1000 cub. ft. of final <i>C</i> -massecuite	—	—
Suprefine X (JACK FROST, Nat. Sugar Ref. Co.) used suspended in alcohol	$\frac{1}{2}$ -1 $\frac{1}{2}$ lb./1000 cub. ft. of final <i>C</i> -massecuite	—	< 20-25 μ
Fondant sugar (Calif. & Haw. Sugar Ref. Co.) used suspended in high grade sugar liquor	$\frac{1}{2}$ lb./100 cub. ft. final <i>C</i> -massecuite	—	< 20-25 μ
FLEISCHMAN, Havana* powdered sugar in alcohol or gasoline	3 lbs. fine sugar/3,600 cub. ft. <i>C</i> -massecuite	—	—
Fondant seed by A.T.J. APPELBOOM ^b	320 ml slurry/750 cub. ft. seed strike 325 cub. ft. seed strike, used for 750 cub. ft. <i>C</i> -massecuite 2 ml alcohol or gasoline + 1 g fondant sugar 140 g sugar/3600 cub. ft. <i>C</i> -massecuite**	—	calc. 5.5 μ det. acc. to publ. 10 μ
Milled sugar in aerogene or gasoline, resp. isopropyl alcohol 140 g sugar + 250 ml gasoline Queensland's technique (a) dry icing sugar ^b	(a) 1 lb./6000 glns. of final <i>C</i> -strike** (b) 80-100 g slurry for 5200 glns. <i>C</i> -massecuite ⁷	70-74	3-5 μ
(b) milled sugar in methylated spirit ⁷	11 lbs. of sugar in 2 gln. of alcohol for 4500 cub. ft. of final massecuite	(a) 73-75 final grain size 0.33 mm (b) 60 syrup 84-88 final grain size 0.62 mm	10 μ 3-4 μ
Cuba, powdered sugar in alcohol as seed ⁸			

* Recomm. Cuba techniques.

** Java technique.

mately 0.05 mm. When this grain size has been reached, the second phase of the boiling process can be started, being the introduction of molasses for filling up the pan.

3. After the introduction of the slurry of finely powdered sugar, it is recommended to keep the mass in active movement and circulation by a lively boiling process which can be sustained during this initial period of growth of the nuclei by the introduction of the so-called movement water.

The significance of the introduction of movement water is that a satisfactory rate of evaporation can be maintained without the danger of having a too high supersaturation involving the formation of secondary grain.

4. The system of graining on powdered sugar in low purity molasses can be standardized by the use of the conductivity control method.

It can be guaranteed, if the prescriptions for this system of graining are followed carefully, that the resulting grain in the footing is uniform, consisting of well-formed regular sucrose crystals, free of complexes, clusters or conglomerates.

As at this moment the literature on this phase of the crystallization technique is growing, some publications are to a certain extent conflicting, respectively confusing in the statements made as to the recommendable technique. It is considered advisable to review the different phases of this crystallization technique.

(b) What Kind of Powdered Sugar Should be Used?

There exist a number of methods to prepare or select a finely divided sugar as the source material for the nucleation in low grade products:

1. One of the oldest systems to get powdered sugar is to collect the fine sugar from the cyclones from sugar driers in refineries and to use this sugar as a dry powder to be introduced in a pan when a sufficient degree of supersaturation has been reached. The experience has shown, however, that the powdered sugar collected in this way is not a uniform product. Furthermore, this system of introduction of nuclei did show that this method usually was not a seeding method but as the sugar was sucked in in a dry state suspended in air, it was actually more a shock seeding method. It was considered that the air as such caused also the formation of nuclei similar to the phenomenon encountered in the graining by string proof boiling.

This method of the selection of the fine grain by using the cyclone dust from refineries is not recommended.

2. It was recommended to use commercial sugars such as Confectioners 6 × DOMINO or 10 × DOMINO from the American Sugar Refining Company,

or 6 × or microfine Super × JACK FROST from the National Sugar Refining Company. These are ground sugars obtained by grinding granulated sugars in hammer mills and screening the sugar through silk bolting cloth or via air separation and cyclones. This product is usually manufactured with 3 to 5% starch in it to prevent caking. But it should also be observed that as to grain size and particularly grain regularity, this type of sugar cannot be qualified as a well-standardized product. The degree of fineness depends on the condition of the mills and the load of mills and screens.

Although the refineries are trying to use always the same raw material, being high grade granulated refined sugar that has been rejected by the screens as too coarse for packed standard fine granulated, it is undoubtedly a fact that there are always differences in the quality of this raw material affecting the degree of fineness of the 'confectioners' or 'icing sugar' as it is usually called. These disparities do not make any difference in the evaluation for practical purposes in cooking, ice cream and chocolate manufacture, etc., but they can be of a fundamental effect as to the resulting grain size when it is used for graining purposes.

Another point that must be observed is that when this 'confectioners' is used for graining as a 'dry sugar' and introduced in the supersaturated sugar solution used for graining, always a considerable number of extra nuclei is formed above the number of nuclei actually introduced via the seed grain.

It has been tried to overcome these difficulties by mixing the icing sugar or fondant sugars with an organic solvent (ethyl alcohol, methanol, isopropyl-alcohol, or gasoline) which prevents first the introduction of air in the pan and, in the second place, when the sugar is well mixed with the solvent, the nuclei develop into well-formed single crystals and prevent the formation of conglomerates which in many cases can be observed when dry powdered sugar is used.

But even under the condition that the fine seed grain is suspended in an organic solvent, it can be observed that the sucrose crystals in the massecuite can differ in size. There is no simple relationship between the amount of sugar used for nucleation and the final number of crystals of a certain crystal size in the final boiling.

3. It has been tried to use powdered sugars by making a slurry with a slightly supersaturated solution of pure refined sugar. Such a solution was made by dissolving a sugar to saturation at a temperature of 35° to 40° C, decanting the saturated solution, heating this solution to 50° C to be certain that no sucrose crystals were left in this solution, cooling this solution to 30° C, being supersaturated at this temperature, introducing in this sugar

liquor a well known amount of fondant sugar and mixing this with a mechanical stirrer to a homogeneous slurry which is used for graining. This is introduced in the pan when a sufficient supersaturation has been reached of the concentrated footing in the vacuum pan. This method properly applied prevents the introduction of air causing extra nuclei formation.

A thorough dispersion of the powdered seed sugar in the sugar liquor is essential to obtain satisfactory results. This has to be mixed in in a mechanical stirrer, f.i., a WARING blender. The amount of icing sugar to be used is approximately 1 kg per 1000 cu.ft. of final massecuite.

It has been stated already, but it must be emphasized, that it is essential that the sugar be mixed and disintegrated homogeneously in the sugar liquor.

If we have to make a comparison between the use of a slurry in an organic

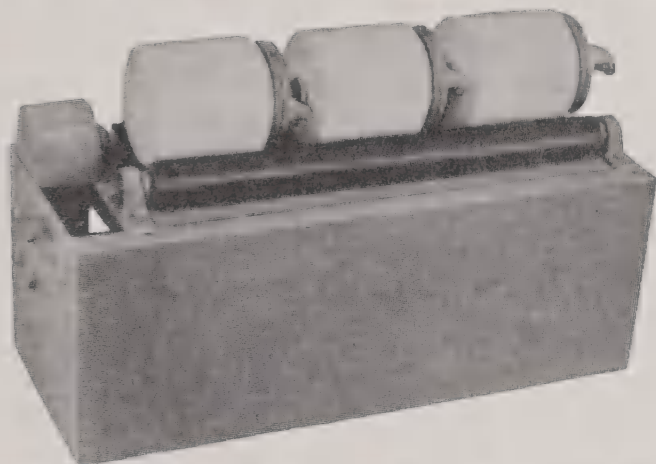


Fig. 7/18. Porcelain jar mill, 2 liter, 30–50 r.p.m. Used: 25–40 steel balls $\frac{3}{4}$ " or 80–120 $\frac{1}{2}$ " flint pebbles, 1 liter gasoline + 250 g high grade coarse refined granulated. Milling time 24 hours. *Final crystal size* 3–4 μ . This type of ball mill was used in Java in most of the sugar mills between 1934 and 1941 for preparing a slurry of seed grain dispersed in gasoline. This kind of ball mill can be constructed by the workshops of the sugar factories. It was customary to have this ball mill somewhere outside the laboratory on account of the inflammability of the gasoline. The volume of the suspension of seed crystals was measured exactly in small bottles, eventually diluted with some extra gasoline, to be used on the pan floor.

It is also possible to order a complete ball mill giving similar results (see Fisher Scientific Catalog 8–413, Minimill, motor driven Fisher ball mill). This type of ball mill is recommended strongly for all sugar factories for preparing a uniform homogeneously suspended slurry of powdered sugar or fondant sugar in an organic fluid.

solvent such as gasoline or propylalcohol, or a slurry in a sugar liquor, we feel that the simplest method is the use of an organic solvent. The disadvantage remains that the uniformity of commercial fondant sugars as the raw material for nucleation is still doubtful. It is for this reason that other methods have been developed.

4. Java has been using a method by grinding refined sugar in a ball mill in an organic solvent. Used was for this purpose coarse granulated refined (as being the product of the greatest purity, low in reducing sugars) which was ground in a simple ball mill in the laboratory as given in Fig. 7/18.

The experience has shown that it was possible by this method of grinding to obtain a product of great uniformity and of which only a small amount had to be used for nucleation.

This method of graining was developed in Java not originally for low product boilings but for the graining of, to the contrary, high grade boilings for manufacturing very fine sugars called in the Far East 'soft sugars' with a crystal size smaller than 0.15 mm, average crystal size 0.10 mm. This sugar product is a special product made for the Chinese market.

The last phase of the manufacturing process for this grade of consumption sugar consists of mixing this very fine sugar with a certain amount of concentrated invert syrup which gives the sugar a sticky character and a velvet touch.

To standardize the graining technique, the method of using finely powdered sugar suspended in an organic solvent for the nucleation was developed. Later on (in 1935) this method was transferred to the graining of low product boilings.

(c) *The Use of Fondant Sugar as Primary Seed for Low Grade Boilings*

APPELBOOM, a sugar technologist in British Guyana, published in 1955 a method⁵ to prepare a fondant sugar as used in the factories of Booker's Sugar Estates, Ltd. The details of this method, called 'fondant graining', are discussed in the following paragraph.

(i) *Manufacture of fondant sugar for full seeding technique according to APPELBOOM*

1. 500 g of (refined) white or high grade washed raw sugar of 99.5 purity is dissolved in water to 60 brix.

2. The sugar solution is carefully filtered through a very fine filter cloth, preferably after the addition of a small amount of kieselguhr.

3. The filtered sugar solution is boiled in a copper or stainless steel sauce pan till a temperature of 116° C is reached, corresponding with a brix of approximately 88*.

* The boiling point of pure sugar solutions under atmospheric pressure at different brix is as follows:

Boiling point in °C	Brix
115.0	86.7
115.9	87.5
116.8	88.2
117.7	88.9
118.5	89.5

4. An invert sugar solution is made by dissolving 1000 g high grade granulated refined sugar in exactly 282 ml. of distilled water. To this solution obtained by heating to a temperature of 85°C is added exactly 2.2 ml diluted HCl (made by diluting 4.3 ml concentrated HCl to 100 ml). This acidified sucrose solution is kept, after the addition of acid, for exactly 10 minutes at 85°C . The temperature is raised to 105°C by heating it in a copper or stainless steel sauce pan and kept at this temperature for exactly 15 minutes. This invert sugar solution is cooled to room temperature and can be kept for an indefinite time as one of the ingredients for making fondant seed sugar.

The amount of acid present in this invert sugar solution is one part HCl per 25,000 parts of syrup.

The pH of this invert sugar solution (determined at room temperature, after dilution 1 : 1, with a pH-meter) has to be 2.7 to 3.0. (depending on the purity of the used sucrose; with purest refined sugar the pH is 2.7, with a refined sugar made with vegetable carbon in Cuba the pH is approximately 3.0).

5. To the concentrated sugar solution as made sub 3 is added 140 g of the invert sugar syrup sub 4. The boiling is continued for exactly 1 to 2 minutes (under no condition longer) till a temperature of 116°C is reached.

6. The mixture is poured immediately into a large container, a stainless steel pan or a large Erlenmeyer flask, and cooled as quickly as possible to 75°C under continuous stirring of the syrup by cooling with cold water.

7. When a temperature of 75°C is reached, the mixture is transferred to a shallow dish pan suspended in a cold water-bath. The syrup is thoroughly mixed and agitated with a putty knife to obtain a rapid cooling and to get a homogeneous crystallization. When the crystallization starts, the mass becomes stiff and gets a fondantlike consistency. When the mass has been cooled to room temperature, it can be transferred to well-closed bottles and kept for several weeks to be used as seed grain for the afterproduct strikes.

8. The fondant sugar is made into a slurry by mixing it in a ratio of 100 g of fondant sugar with 200 ml of alcohol. It is essential that this mixture be disintegrated homogeneously in the alcohol, preferably by stirring it in a ball mill as will be described later. The mixture must be stirred for at least one hour.

This alcoholic sugar suspension can be kept in stock for a limited time to be used as seed slurry. A certain amount of recrystallization takes place and the smallest crystals disappear. The average crystal size of this slurry increases with the time of storage.

9. The amount of seed slurry to be used is approximately 40 to 50 ml per 100 cu. ft. of seed strike.

10. A seed strike is a strike that is used as a footing for the final *C*-massecuite. It is customary that the amount of seed strike footing used for a final *C*-massecuite is approximately $1/3$ of the final massecuite volume. This means that the amount of seed slurry to be used per 100 cu.ft. of final *C*-massecuite is approximately 15 ml.

(ii) *Comments on the method of making seed grain according to APPELBOOM*

1. It is mentioned in the paper by APPELBOOM that the preparation of a seed slurry, starting with the 60-brix sugar solution and invert syrup, takes only 30 minutes. This is optimistic. Concentrating a 60 brix sugar liquor in a laboratory pan to a boiling point of 116°C takes approximately 30 to 40 minutes. The actual time required by an experienced laboratory chemist, requiring his personal attention all the time, takes $\pm$ five quarters of an hour.

2. The preparation of the invert syrup must be done with certain precautions to have no overheating of the solution to be inverted and to have minimum of color formation.

The original sucrose liquor has a brix of 78. After inversion and maintaining for 15 minutes a temperature of 105°C , the brix is between 83 and 86. When this invert sugar solution is cooled to room temperature, it should be a transparent light yellow syrup; the viscosity is high; it resembles a very viscous honey.

3. When as prescribed for the manufacture of fondant sugar 140 g invert syrup has to be used, it is possible to weigh out exactly this amount of syrup. But to blend it in *quantitatively* in highly concentrated sugar liquor is not so simple. There are always some losses of syrup adhering to the container in which the syrup has been weighed. The simplest way is to use a nickel sugar capsule as weighing dish.

According to analysis, the amount of invert sugar in this invert syrup is more than 95% reducing sugars % brix. This means that in using 140 g of invert of approximately 84 brix, the amount of reducing sugars added to the sugar liquor equals approximately 115 g.

4. For the manufacture of the fondant sugar, 500 g of *white* or *high grade raw sugar* is used. This means that the amount of reducing sugars *added* in the form of invert syrup is on the total amount of solids in the finished product 18.7%.

We have been using for making fondant sugar pure refined sugar (DOMINO fine granulated). This was brought to a boiling point, as prescribed, after the addition of the invert syrup of 116°C . The blending in of the invert syrup took approximately 2 minutes to have the cold invert syrup distributed homogeneously in the hot concentrated sugar solution.

When this mixture is poured into a large Erlenmeyer flask and cooled to 75°C , it is practically impossible to transfer this cooled mass without considerable losses to a shallow metal bowl. The simplest way is to pour the solution directly after the temperature of 116°C has been reached into a wide stainless steel pan with a diameter of 11" to 12", put pan plus content in cold water and cool the whole mixture under constant stirring to the beginning of crystallization. The stirring can be done with a heavy wooden ladle till the crystallization starts and is continued till the whole mass is solidified.

5. The resulting crystallized mass has a soft creamy texture. Theoretically the invert sugar content on dry solids had to be 18.7 %. The actual reducing sugar content in a sample was 16.2% on fondant sugar; water content 13.7; reducing sugars % solids 18.8.

6. The pH of the invert syrup was approximately 2.8. The pH of the fondant sugar dissolved in water 1 : 1 was approximately 4.8. At this pH and the used temperature, the rate of inversion is rather high. At a pH of 4.5, the inversion rate at 105°C is approximately 10% per hour. At 115°C , it is approximately 30%, or per minute 0.5% of the sucrose present is inverted. The risk of inversion during the manufacture is high. A question is whether it is recommendable to use high grade refined sugar as raw material. APPELBOOM in his publication does not mention refined as raw material but recommends the use of white sugar. This may be plantation white or a high grade raw sugar.

In using a high grade raw and a polarisation over 98, we had under identical conditions as to the quantities of raw material to be used that the pH of the mixture of concentrated raw liquor and invert syrup was approximately 6.0. The inversion rate of this mixture heated to 116°C is only a small fraction of what is found with pure refined sugars. The percentage of reducing sugars in the fondant sugars was 18.2% on solids.

7. APPELBOOM mentions that the slurry is prepared by mixing 2 ml of alcohol per g of fondant. He mentions that '*alcohols* are suitable for preparing a slurry of the right consistency for seeding'.

When we are mixing 100 g of this fondant sugar with 200 ml of technical isopropyl alcohol (91%), it is practically impossible by just shaking this mixture in a well-closed bottle to get a homogeneous distribution of the fondant sugar. It remains in large lumps*. Also by mixing in a mortar with

* The fondant sugar consists of fine sucrose crystals surrounded by a sugar saturated invert syrup. The analysis of the sample of fondant sugar was: 13.7% water; 16.2% reducing sugars; real sugars % water = 118.

The solubility of sucrose in this invert syrup is at 30°C 175 sucrose per 100 parts of water or for the sample under consideration 24.0% sucrose in solution.

The fondant sugar according to this analysis consists of 46.1% crystals and 53.9% syrup, having a composition: 25.4% water" 30.1% red. sugars; 45.5% sucrose.

alcohol, it is not possible to get an equal distribution. We have to put a big question mark whether this system of preparing seed is the simplest solution we have available at present.

8. Microscopic observation of the grain did show that the fondant sugar exists of a mixture of crystals of heterogeneous size. The regularity of the individual crystals is excellent. The average grain size is, however, much larger than can be deducted from the description in the paper by APPELBOOM. The average grain size is larger than what is found in a Confectioners 10 $\times$ of the American Sugar Refining Co.

Further experimentation is required to be certain that APPELBOOM's method is the best technique for obtaining uniform constant seed grain for the afterproduct boilings in canesugar mills.

(d) *Standard Technique for Making a Slurry of Seed Grain in Organic Solvents by Milling*

The technique for obtaining a uniform seed grain by milling granulated sugar in an organic solvent was developed in Java in 1934/1935 and described in the sugar technical literature for the first time by ALEWIJN, technologist of the Java Sugar Experiment Station⁹.

The first technique consisted of grinding 25 g of high grade coarse refined sugar in 90 ml aerogene. This grinding was done in ordinary widemouth French square sugar sample bottles by adding 5/32" diameter steel balls. For one filling of a sugar bottle were used 500 to 600 steel balls weighing 140 to 150 g. Number of revolutions 75 per minute. Time of grinding 12 to 24 hours. Final crystal size of the ground sugar 0.003 mm.

In later experiments the system of grinding was improved by using a regular ball mill in porcelain and replacing the steel balls by marbles, porcelain or flint pebbles, or pyrex jars with a clamp top or spring cover clamp have been used. The rubber gasket had to be made in a special grade of rubber when gasoline was used as dispersing fluid. The ratio of sugar and solvent was increased, and later on was used 30 g of refined sugar per 100 ml of organic solvent.

A large number of organic solvents have been tried out (Table 11). It was found that the best results were obtained with a seed suspended in an organic fluid with a boiling point lower than the boiling point of water.

The introduction of this slurry in the pan resulted in a kind of explosive disintegration and perfect distribution of the slurry in the supersaturated sugar solution with no formation of conglomerates whatsoever. The same result is obtained by suspending the fine sugar in gasoline, but some of the

gasoline fractions, when they are high in aromatics as for instance from Borneo, can give a certain odor to the sugar which could be detected after very careful examination. This is not the case with American and Cuban gasoline being low in aromatics. But some of the gasoline as made in the Far East is high in toluene and xylene, which have a penetrating odor which

TABLE 11

Solvent	Boiling point in °C	Specific gravity
Benzene (C ₆ H ₆)	80.1	0.87
Toluene (C ₆ H ₅ CH ₃)	110.8	0.87
Xylene (C ₆ H ₄ (CH ₃) ₂) (o, m or p)	138-144	0.86-0.88
Carbon tetrachloride (CCl ₄)	76.7	1.58
Methyl alcohol (wood alcohol)	64.6	0.79
Ethyl alcohol (95 to 99.5 %)	78.3	0.78
Isopropyl alcohol	82.4	0.78
n-Propyl-alcohol	97.5	0.80
Acetone	56.1	0.79
Aerogene or lighter fluid, being a mixture of pentane, hexane, heptane, octane	36.0 } 78.6 } 92-98 } 125.6 }	0.65-0.70
Gasoline, being a mixture of hexane to nonane	45-195 °C (110-380 °F) (medium boiling point 128° C or 261° F)	

could be detected even in extremely small traces in plantation white sugar.

In the use of gasoline, it is recommendable always to check the volatility of the aromatic substances in the gasoline via a practical boiling test by introducing approximately 1 liter gasoline in a pan and see whether this gasoline can be detected by its odor in the massecuite in the crystallizers or in the sugar coming from the centrifugals. The best way to detect traces of aromatics in sugars is not by smelling, but by actual tasting and to take a spoonful of sugar in the mouth and see whether a faint taste, resembling the sense effect of kerosine, respectively a poor quality of gasoline, can be detected. The experience is that this is not the case with U.S. gasolines. They can be recommended if they pass this test, without any objection, as suspending fluid for making a slurry of fine sugar to be used as seed grain.

(e) *Systems of Grinding Sugar in Organic Fluids to be Used as Seed Grain*

Among the recommendations in the sugar literature are the use of methylated spirit (Queensland), pure ethyl alcohol (95 %) (British West Indies), water-

free alcohol ($> 99.5\%$) (Java), gasoline (Java) and isopropyl alcohol (Hawaii).

The *Australian* method for making seed slurry was as follows: 2 pounds of I A granulated refined are suspended in 2 liter of methylated spirit. Ground in an one gallon pyrex bottle, 200 revolutions per minute, grinding time 24 h. As grinding material were used 24 $7/8$ " steel balls. It was possible with this slurry to make 20 grainings for *C-masseccutes*, each of 5,200 glns. of a purity of 60. It was customary to use 20 to 100 g of sugar slurry per boiling.

The *Java* method was:

(a) Sugar ground in gasoline; 140 g sugar and 250 ml of gasoline ground in a 500 ml pyrex bottle with 80 $1/2$ " steel balls for 24 hours. This slurry was used in total for graining the footing for 3600 cub.ft. of *C-masseccute*. The average grain size of the seed slurry was 3 to 5 μ .

(b) It is possible to get an extremely fine grain by grinding sugar suspended in gasoline in a modified blender. Used was a 250 ml widemouth bottle, containing 510 $5/16$ " and 750 $1/8$ " steel balls, total weight 370 g. As stirrer was used a steel shaft with a propellor of 15 mm. Number of rotations 1000 per minute. The bottle had to be placed in a cold water-bath to remove the heat developed during the grinding process. Grinding time 3 hours. Final size of the disintegrated sugar crystals 0.5 to 3 μ . Average crystal size 2 μ .

The experience is that when the seed crystals are of an extreme fineness and the supersaturation of the sugar liquor to be ground is not high enough, the very fine grain is dissolved and does not act as nuclei. It has been found that the solubility of the finest fraction in icing sugars can be to 4% higher than the solubility of sucrose of normal crystal size (increase in refractive index 0.0022)¹⁰.

Used was 100 ml of this suspension (2 μ crystal size), made by using 25 g of sugar and 200 ml gasoline for 1000 hl masseccute, as a footing for *C-boilings*, or 12.5 g of seed per 100 hl of footing of an average crystal size of 0.1 mm, which was used in a ratio 1 : 4 for making the final *C-masseccute*. We have reached in this case the limit of fineness for seed grain by simple milling methods in the laboratory.

The system of disintegrating sucrose crystals by a mechanical stirrer and the use of steel balls as milling medium makes it possible to obtain an average grain size somewhere between 1 and 2 μ . A part of the sucrose crystals has been disintegrated to a linear grain size of 0.3 to 0.5 μ .

This system is, however, not recommended for the boiling technique in raw sugar mills. It is in the first place an objection that the amount of seed grain to be used becomes too small. We have to give consideration to the

fact that a certain amount of liquid slurry has to be drawn in the vacuum pan, which always involves some losses in the pipe connections. It is necessary, when a certain volume of this slurry is used, that we are certain that 95% of the measured volume is actually distributed homogeneously through the pan content. It is for this reason, with a proper dimensioning of intake funnel, valve and pipe connection, that the *minimum amount of slurry* to be used should be 100 to 250 ml for a footing (see Fig. 7/21).

(f) *Different Techniques of Grinding*

The first system used for grinding sugar used as seed grain in Java is given in Fig. 7/18. A widemouth bottle was filled with gasoline, refined sugar and a certain number of steel balls; this was rotated on a motor driven revolving wooden roller at the same time acting as carrier and support for the bottle. This is a simple construction made in the workshops of the sugar mills, requiring no special equipment. It was possible with this equipment to obtain a regular grain with an average grain size of 3 to 5 μ .

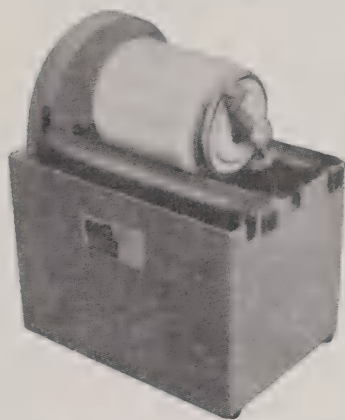


Fig. 7/19. Flint pebbles, diameter $\frac{1}{2}$ "– $\frac{3}{4}$ "; 80–120 r.p. min. Type of ball mill as can be used for grinding granulated refined sugar to a homogeneously suspended seed slurry to be used for complete seeding of *C*-boilings.

This kind of ball mill can be ordered as a unit (see Fisher Scientific Catalog 8-372, Single, specimen ball mill, with motor).

When this type of ball mill is ordered, it must be ordered with 2 extra porcelain jars, 2 extra caskets, and with a complete set of steel balls and flint and porcelain pebbles, $\frac{3}{8}$ ", $\frac{1}{2}$ " and $\frac{3}{4}$ " diameter. Of each of this grinding material must be ordered 2 lbs.

Other factories have been using a commercial type of ball mill as given in Fig. 7/19.

It has to be stressed at this point that the grinding technique to obtain a uniform seed grain is not as simple as it may seem. Consideration must be given to:

(a) The number of revolutions and the size of the bottle or jar used for the grinding process.

The following approximate data as to the dimensions of jar or bottle and the circular outside speed of the rotating grinder have to be followed (Table 12).

TABLE 12

Volume in ml of sugar slurry to be made per grinding	Inside diameter jar or bottle		Circular speed per minute	Number of revolutions per minute
	in inches	in cm		
600-700	4.5	11.5	30-45	80-120
1000-1500	8.8	22	40-50	60-75

When greater speeds are used, the grinding effect is reduced instead of increased.

(b) The number of grinding medium (steel balls, marbles or pebbles).

It was found that per liter of *bruto* volume of the grinding bottle or jar had to be used 15 to 25 $3/4$ " steel balls or 30 to 50 $3/4$ " pebbles. In the forming of steel balls, it is recommendable to use per bruto liter of volume approximately 500 g of steel balls or 400 g of pebbles or marbles. The filling of the jar or bottle with a mixture of sugar and organic fluid must be 50% of the bruto volume of the bottle. Greater amounts of grinding medium in the form of steel balls or pebbles is not recommended because otherwise the heat development may cause pressure in the bottle and the stopper or cover may be loosened up.

In using organic fluids, it is recommendable to use either a stopper ground carefully in the mouth of the bottle or a cover tied to the opening with a clamp.

It is recommended to prepare the standardized sugar slurries in the laboratory and to make a number of bottles with the exact volume in uniform concentration of sucrose in the laboratory to be used on the pan floor. With organic fluids, it is possible to prepare these seed slurries a long time before they have to be actually used. With the use of gasoline, isopropyl alcohol or absolute alcohol (> 99.5% ethyl alcohol), these slurries can be kept without any change in their characteristics for 3 months.

It is recommendable to make the seed slurries for each graining operation not smaller than a net volume of 150 ml. If the seed is too small according to the amount of footing to be made for a certain final volume of *C-masse-cuite* according to the dimensions of pans, seed mixers and the final volume

of the seed pans this volume must be made by diluting the seed grain suspension with a proper amount of organic fluid.

Question: What are the objections against the use of commercial confectionary or icing sugars as seed for the C-boilings?

Icing sugars cannot be qualified to be uniform as to grain size. The commercial requirement as to the fineness of the sugar is that it has to pass through a 200 mesh sieve having an opening of 0.074 mm.

The old practice that icing sugar had to be made by screening it through silk bolting sieves of 325 mesh has been eliminated in most U.S. refineries. The present sugar is made by grinding and air separation, and collecting and classifying the fine pulverized sugar in cyclones. But even in using sieve 325 mesh, it must be realized that the sieve opening is still 44 μ . Using the finest commercial screens, the 400 mesh bolting sieves applied for mechanical screening in the technique, we are still dealing with a screen opening of 37 μ .

Calculating with these screen openings or determining the grain size via microscopic measurements we have to come to the conclusion that the amount of powdered sugar that must be used to obtain *complete* seeding of a C-strike amounts to several pounds per strike.

Calculated required amount of seed grain for full seeding of low grade boilings: Per 100 hl of final C-massecuite, the quantity of sugar in crystal-line form recovered is 6000 kg. For a linear crystal size of 0.30 mm, the number of sucrose crystals in this quantity is 220×10^9 ; for size 0.35 mm, 150×10^9 .*

The number of sucrose crystals per mg is for the following linear crystal sizes as follows (Table 13).

TABLE 13

	Linear crystal size	Number of crystals per mg
Coarse icing sugar	40 μ ($\pm$ 325 mesh)	12,000
Standard icing sugar	$\left\{ \begin{array}{l} 20 \mu \\ 10 \mu \end{array} \right.$	$\pm 100,000$ $\pm 800,000$
<i>Wet milling in alcohol</i>		
Sugar obtained by wet milling process	$\left\{ \begin{array}{l} 5 \mu \\ 2-3 \mu \end{array} \right.$	$\pm 6-7 \times 10^6$ $\pm 50 \times 10^6$
Final product of wet milling	$\left\{ \begin{array}{l} 1-2 \mu \end{array} \right.$	$\pm 400-500 \times 10^6$

* This has been calculated assuming the weight of a sucrose crystal 0.30 mm linear size = 0.029 mg; 0.35 mm linear size = 0.048 mg. The number of crystals per mg is 34, respectively 21.

In Table 14 we give the amount of seed sugar required in g per 100 hl final *C*-massecuite.

TABLE 14

Seed grain, linear size in μ	Amount of seed in grams/1000 hl massecuite (350 cub. ft.; 3600 U.S. glns)	
	for 0.30 mm <i>C</i> -sugar	for 0.35 mm <i>C</i> -sugar
40	$\pm$ 16,000	$\pm$ 10,000
20	$\pm$ 2,000	$\pm$ 12,000
10	$\pm$ 200-250	$\pm$ 150-180
5	$\pm$ 30-40	$\pm$ 15-25
2-3	$\pm$ 3-6	$\pm$ 2-5
1-2	$\pm$ 0.5-1	$\pm$ 0.3-0.6

It is for this reason that with the use of powdered sugar, even as it is used today and even when it is applied in the form of a slurry in alcohol, the

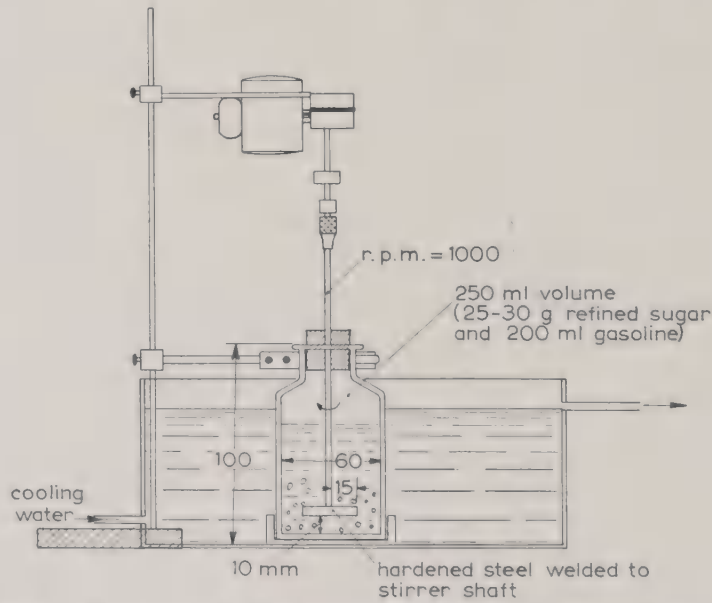


Fig. 7/20. Used: 370 g steel balls $\frac{1}{11}$ " and $\frac{1}{8}$ ". Grinding time 3 hours, linear size 0.5-5 μ (average 2); grinding time 7 hours, linear size 0.5-3 μ (average 1-2). System of grinding to obtain in a reasonable short time an extremely fine seed slurry. The disadvantage of this system is that the heat development is high and the whole system has to be placed in a cooling bath. The finest seed slurry has been made with this system of grinding. It was possible to make *C*-strikes with complete seeding in standard vacuum pans (200-250 hl, or 700-900 cub. ft.) with 10 to 50 g of seed grain per strike.

system of seeding remains a combination of true seeding and shock seeding. In the past, investigations have been made on this subject as to the amounts of nuclei that have been formed by introducing small crystals in a super-saturated sugar solution. The experience in Java and Australia with pow-

dered sugars of different origins was that the amount of final crystals in the finished massecuites was 10-30 fold the number of crystals introduced in the pan via a dry powder or in the form of an alcohol slurry. In Queensland, KELLY made a special investigation on this subject. KELLY has been using confectioners powdered sugars; he found that in graining low product

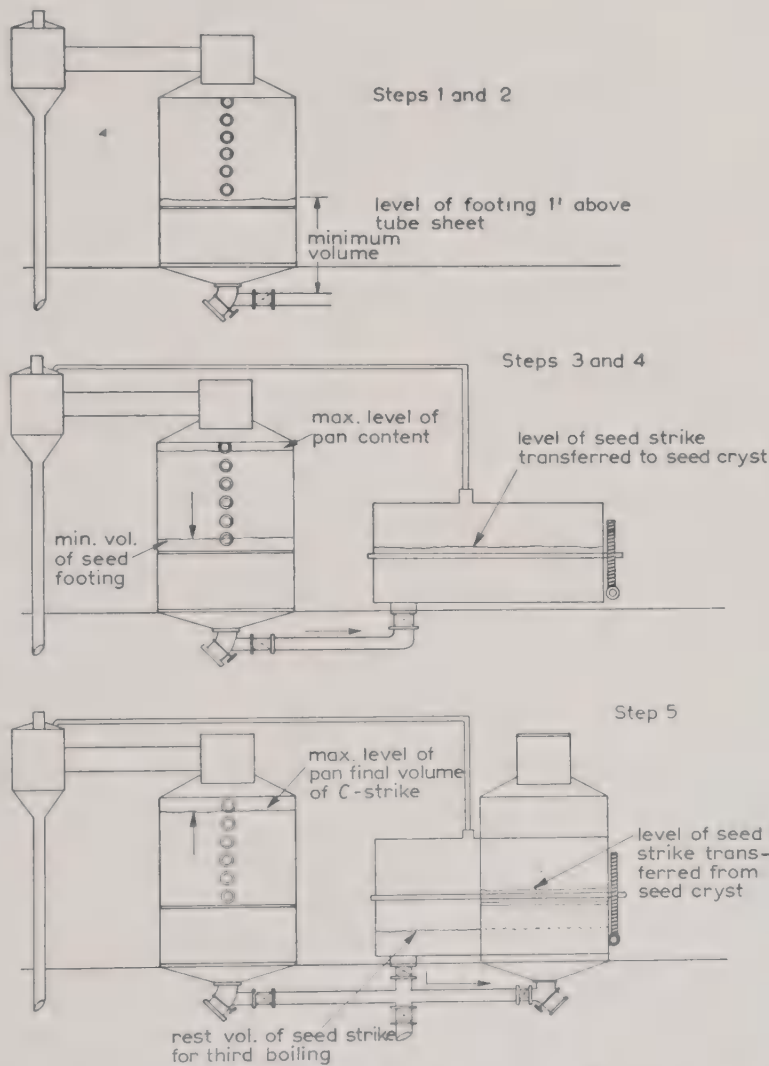


Fig. 7/21. The following processing steps in the making of third strikes in raw sugar mills have to be distinguished:

1. The concentration of the raw material to be used for nucleation or seeding. This is preferably *A*-molasses with a purity of 70-75. The purity level must be adjusted by mixing in a certain amount of syrup or *B*-molasses, depending on the purities of syrup and molasses of the factory.
2. The introduction of seed slurry when a required supersaturation has been reached to be followed by the maturing or ripening of the introduced seed to a visible crystal size which has to be 0.05-0.08 mm linear.

- 3 Boiling of the seed strike This is done by continuous intake of *A*-molasses to a final purity of the seed strike of approximately 65. The grain size increases during the boiling process to 0.12–0.18 mm linear.
4. Cutting the seed strike. A certain amount of the seed strike is transferred to the seed crystallizer. Enough seed strike is left in the pan to cover the upper tube sheet; this is used for a footing for the final *C*-strike. The intake consists of *B*-molasses, resulting in a final purity of the *C*-strike of approximately 60.
5. In another pan, enough seed strike from the seed crystallizer is introduced to cover the upper tube sheet. This footing is boiled with *B*-molasses to a second final *C*-strike. Depending on the ratios of the minimum volume of the pans and the final volumes, it will be possible to boil from one seed strike to three or four final *C*-strikes. The use of a seed crystallizer adds to the elasticity of the processing of the pan floor and can increase tremendously the efficiency of a pan station because time losses resulting from the required synchronization of the ends and beginnings of processes can be eliminated.

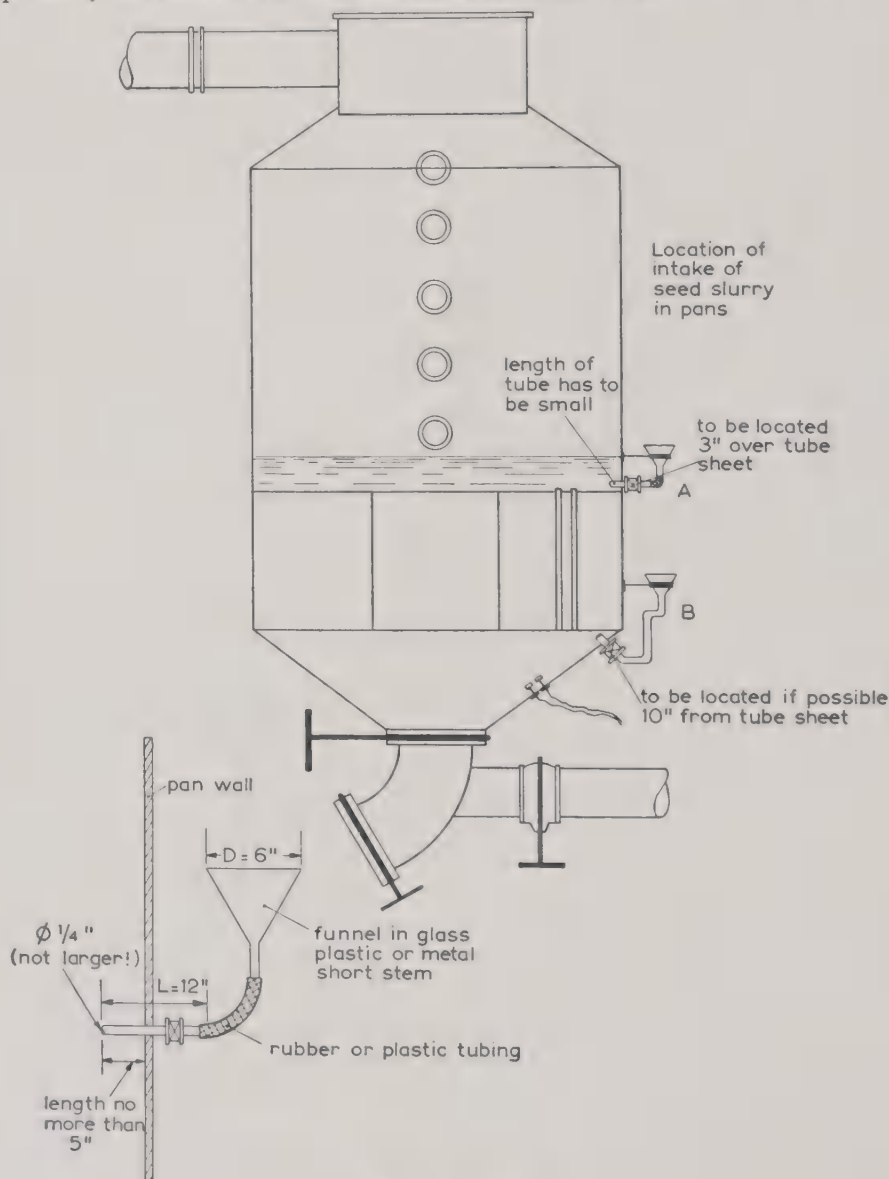


Fig. 7/22.

boilings (purity between 70 and 75), 17 new crystals were formed for every one introduced. But even with these extra nuclei formed in the very first beginning (the first 1 or 2 minutes after introducing of seeding to the pan), precautions had to be taken that no new nuclei were formed during the growing process, what is named 'false grain formation' or the 'formation of secondary grain'. It was essential that the surface area of the crystals were maintained at a minimum figure relative to the quantity of the mother liquor and this related to the supersaturation. It was possible to put it in a quantitative form expressed by the following relationship:

$$A = \frac{19x}{L(100 - x)} \cong \frac{a (\text{degree of supersaturation})}{P^{1.4}}$$

where

A = area of sugar in m^2 per unit of mother liquor (1 liter)

x = degree of supersaturation

L = average length of linear size of crystals expressed in mm

P = true purity; purity range for which the formula is valid = 50 to 75

At a supersaturation 1.3, the constant $a = 30,000$

It is for this reason that the present technique for seeding low grade boilings is still in many sugar areas in a state of confusion as to the actual processes taking place in the seeding of pans.

The question came up which organic solvent has to be used. It is desirable that the solvent has practically no solubility for sucrose. Experiments taken with ethyl alcohol of different water contents of 90 to 99.5 did show that the stability of the colloidal sugar was reduced with an increase in the water content. Absolute alcohol is not a product that is generally available in sugar mills, and the preparation of absolute alcohol by distillation is a

TABLE 15
SOLUBILITY OF SUCROSE IN ETHYL ALCOHOL

Vol. % alcohol	SCHEIBLER ¹¹			PELLET ¹²				
	0° C	14° C	40° C	0° C	10° C	20° C	30° C	40° C
90	0.7	0.9	2.3	0.7	0.8	1.1	1.6	2.3
97.4	0.1	0.4	0.5	0.08	0.15	0.25	0.36	0.50
SOLUBILITY AT 14° C								
Weight % alcohol			% sucrose		% alcohol			
90			0.95		89.15			
95			0.15		94.85			
100			0.0		100			

technique in many cases too complicated for the laboratory practitioners, also considering the available laboratory equipment, to give satisfactory results.

In Table 15 we give the solubility of sucrose in alcohol.

We have been trying in Java different other organic solvents, and definitely the choice was the use of gasoline because this is available at all sugar mills. The price is low. The only disadvantage is that it is inflammable. It is for this reason recommendable to do the grinding process somewhere outside the laboratory.

Later on it was GILLETT who recommended specifically the use of isopropyl alcohol, having a low boiling point and giving a good distribution of the introduced slurry in the supersaturated sugar solution. It is a duty-free product that can be ordered by any sugar mill. The only disadvantage is that in a number of sugar producing areas, isopropyl alcohol is not a commonly available organic solvent obtainable directly from local dealers. Furthermore, technical isopropyl alcohol is 91%. It can be obtained 95% or anhydrous but it has to be ordered specifically. The technical isopropyl alcohol has a measurable solubility for sucrose, greater than the solubility in 95% ethanol.

Comparing the price with gasoline, the price is usually considerably higher. Price of technical isopropyl alcohol in the U.S.A. is $\pm$ \$ 2.—; in Cuba and the Dominican Republic per gallon $\pm$ \$ 4.—. Gasoline is \$ 0.35 to \$ 0.50 per U.S. gallon.

(g) *A New System of Special Seeding of the Footing to be Used for C-strikes*

The amount of seed introduced in the form of a slurry in a footing of *A*-molasses is extremely small when a fine pulverized sugar in an organic solvent is used. Assuming that the minimum volume for a footing for the *C*-strikes in the pans as installed in the factories is 100 hl (350 cu.ft.), we have found that it is possible that a seed slurry made by grinding a granulated refined sugar can be reduced to sugar quantities less than 50 g.

As it has been stated above, *extremely small quantities* of a very fine seed slurry are not recommendable since the correct dosage becomes different. On the other hand, it must be realized that the commercial powdered sugars sold as Confectioners Multi X by the American Sugar Refining Company and by the National Sugar Refining Company are rather coarse and require a considerable quantity of seed slurry to obtain complete seeding or, if this is not done, we are always dealing with secondary grain formation. The quantities of sugar in the different phases of the crystallization process specifically for *C*-strikes have been summarized in Table 16.

TABLE 16

RELATION BETWEEN NUMBER OF SEED CRYSTALS, SIZE OF SEED AND CRYSTALS IN SEED STRIKE AND FINAL C-MASSECUITE.

Processing step	Footing or strike	Purity of pan content	Crystal content weight % vol. massec. kg/hl massec.	Average linear crystal size in mm	Number of crystals per kg of sugar	m ² crystal surface per kg sugar	m ² crystal surface per hl massecuite	Number of crystals per hl of massecuite
1. Introduction of seed slurry in supersaturated footing	100 hl	70-75	0.02	0.005-0.04	$12-1000 \times 10^9$	100-350	0.1-1	$240 \times 4000 \times 10^6$
			0.001	0.003-0.004	$12-35 \times 10^{12}$	1000-2000	1-2	$1000-2000 \times 10^7$
2. Maturing of seed strike footing to the beginning of intake of molasses	100 hl	70-75	20-40	0.10 -0.15	$300-400 \times 10^6$	25-40	900-1200	$1000-2000 \times 10^7$
3. Finishing seed strike to final volume	ratio footing/strike 1 : 3 300 hl	65-70	50-55	0.12-0.18	100×10^6	20-25	800-1000	4000×10^6
4. Boiling of seed strike to final C-molasses of C-strike	ratio seed footing to strike 1 : 3 300 hl	60	60	0.30-0.35	$21-35 \times 10^6$	11-14	600-800	1200×10^6

The slurry of pulverized sugar has by its great fineness a great specific surface area (m^2 per kg of sugar); but it has to be realized that directly after the introduction, the amount of sugar in kg able to crystallize on the available surface area per hl (or cub. ft.) is the first ten minutes very small.

The rate of crystallization ($\text{mg}/\text{m}^2/\text{min.}$) is under uniform conditions

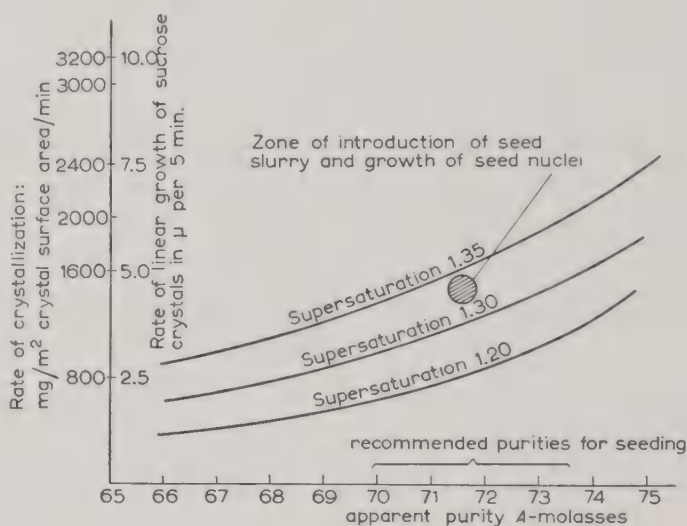


Fig. 7/23. Rate of crystallization of *A*-molasses under standard conditions in canesugar mills. Temperature $74\text{--}78^\circ\text{C}$, concentration 85–87 brix, vacuum 4–5" abs.

of temperature, supersaturation and purity proportional to the time of crystallization. According to determinations made, the rate of crystallization is independent of the crystal size. It is common to express the rate of crystallization as the amount of sucrose in mg going from the solution into crystalline form per m^2 of crystal surface area per unit of time. Usually for the unit of time to express crystallization rate, the minute is taken.

In Fig. 7/23 we have given the rate of crystallization for *A*-molasses in canesugar mills as determined as an average in a number of Java mills. It has to be mentioned in this connection that the rate of crystallization for the same purity of the molasses can show considerable differences from factory to factory. Specifically the reboiling of the molasses in the *A*-boilings (or circulation of nonsugars in the boiling process) can affect the rate of crystallization tremendously.

It is also possible to express the rate of crystallization or the increase in linear crystal size per unit of time. A crystallization rate of 1600 mg per m^2 per minute corresponds with an increase in the linear crystal size of $1\ \mu$ per minute. We can calculate in this way the increase of the amount of sugar in crystalline state per minute, the increase in the surface area per minute

and we are also able to calculate, when we are familiar with the quality of the molasses we are dealing with in our factories as to its crystallization characteristics, the time that is required to make footing.

In Table 17, we give an example of such a calculation.

TABLE 17

SUPERSATURATION OF MOLASSES 1.30-1.35; PURITY 72; RATE OF CRYSTALLIZATION 1500 MG/M²/MINUTE; SEEDING WITH PULVERIZED SUGAR IN ORGANIC SOLVENT

Time after seeding in minutes	Used 1 g seed grain/hl, average crystal size in μ	Surface area in m ² /kg	Weight of cryst. sucrose per hl in g	Surface area per hl in m ²
0	3	1400	1.0	1.4
5	8	500	20	10
10	13	320	80	26
15	18	230	210	48
20	23	180	460	83
25	28	145	800	116
30	33	124	1200	149
35	38	100	1900	200
40	43	94	2600	244
45	48	85	3600	313
50	51	79	4900	390

The time required for ripening or maturing introduced seed nuclei to a sufficient grain size and also to a sufficient concentration of sugar crystals per unit of volume massecuite (or footing) before the pan boiler can start with the intake of *A*-molasses for the second step in the boiling process, namely filling up the pan, can be considerable under certain circumstances. All depends on the rate of crystallization of the material used for the footing.

In the literature, it is mentioned frequently that the purity for the footing recommended is even 65. Our personal experience is that a too low purity increases tremendously the time required for making the footing for the seed strike; preferred is a purity around 72 to 74. This footing guarantees that there is no risk for the formation of clusters or conglomerates; there is a satisfactory growth rate of the nuclei and usually it is found with a normal quality of molasses that the formation of a satisfactory grain size in the footing can be done in 30 to 40 minutes from the moment of the introduction of seed slurry.

The initial size of the grain in the seed slurry is extremely important as to the quantity of sucrose to be introduced and also as to the time required for the making of the footing.

Using a powdered confectionary sugar with an average grain size of

15 μ (which is a small average grain for confectionary sugar), we are usually saving at least 10 to 15 minutes compared to the graining with seed slurry made by wet milling. But, on the other hand, it has to be realized that the amount of powdered sugar to be used must be 100 to 200 times the amount of sugar to be used as milled sugar in an organic solvent. The effect of the initial grain size and also as to the amount commonly used is illustrated in Table 18.

TABLE 18

Graded with pulverized sugar ground in organic solvent		Seeding with icing sugars	
average linear crystal size in μ	amount of sugar per hl of footing	average linear crystal size in μ	amount of sugar per hl of footing
3	1 g	15	10 g
5	5 g	30	80 g
10	35 g	50	350 g
25	1.5 kg	100	2.8 kg
50	5 kg	150	10 kg
100	35 kg	200	18 kg
		250	40 kg

(h) *When must the Seed Slurry be Introduced in the Pan?*

In Figs. 7/24–7/26 we have reproduced recorded conductivities of a Cuban raw sugar factory. In Fig. 7/24, the time from the moment that the seed slurry was introduced till the beginning of the continuous feeding of the footing with *A*-molasses was in this case only 14 minutes. The introduced seed had grown to a size giving a milky appearance to the footing, but individual crystals with well-developed form could not yet be observed.

In this case, the time of maturing is too short and also a defect is that the intake of water during the ripening period was too great, causing a decrease in the degree of supersaturation, respectively a reduction in the rate of crystallization. This kind of boiling has an extremely great chance of forming a secondary grain in the second phase of the boiling process.

In Fig. 7/25, a second example is given of graining in *A*-molasses. The introduction of movement water was restricted during the first 5 minutes after the introduction of the seed slurry (*A*–*B*). After that, the amount of movement water was increased but too liberal. Also in this case, the time for the ripening of the introduced seed, being only 18 minutes, is extremely short. The crystal concentration when the second phase of the boiling process, being the intake of *A*-molasses to fill up the pan, started was still very low.

In Fig. 7/26, we give an example of recorded conductivities for a proper way of graining of a footing of *A*-molasses. The concentration of the *A*-molasses after introduction of seed slurry is by a well-adjusted introduction of movement water kept for 20 minutes at a constant value. At that moment, the introduction of a small amount of *A*-molasses was started,

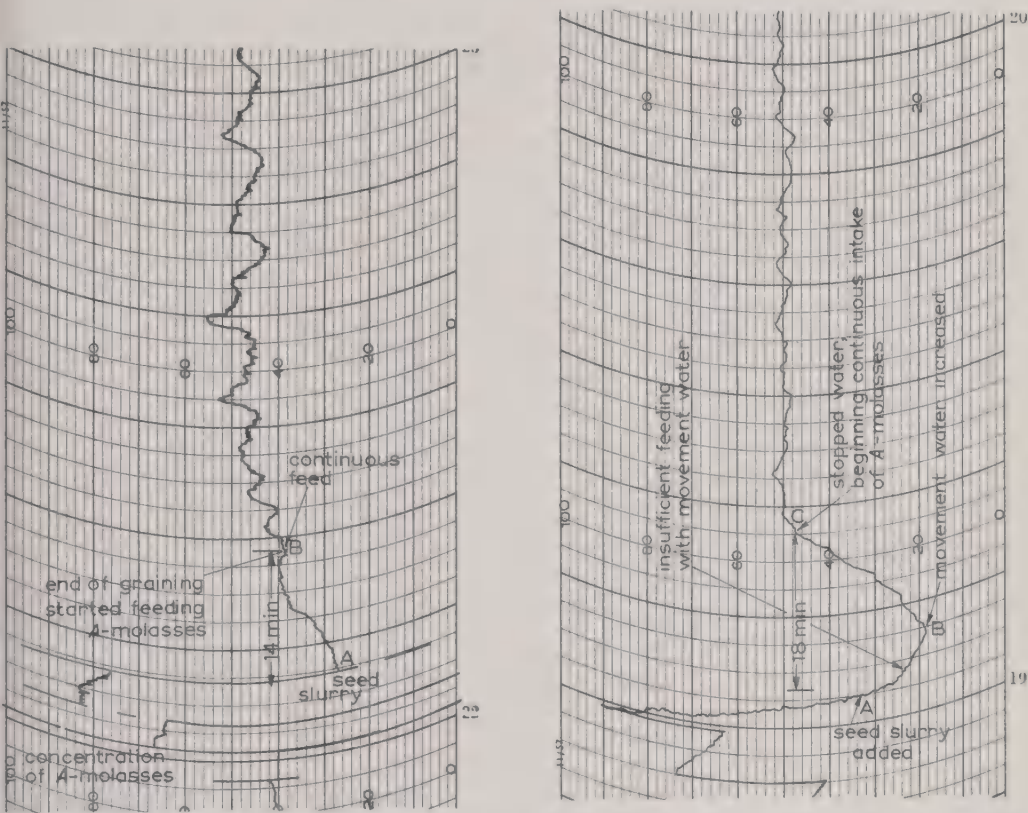


Fig. 7/24. Recorded conductivities in making the footing of a seed strike on *A*-molasses. Seed slurry introduced at A, movement water admitted at the same time. End of ripening of introduced seed at B.

Introduction of movement water in pan stopped and started with feeding of *A*-molasses. Fig. 7/25. Recorded conductivities in making the footing of a seed strike on *A*-molasses. Seed slurry introduced at A. Seed slurry consisted of DOMINO icing sugar suspended in alcohol.

The amount of movement water charged in the pan was too restricted. Supersaturation increased during the first phase of ripening. Movement water increased at B.

continuing the intake of movement water. The whole period for the graining was in this case 25 minutes. The seed slurry used was confectioners icing sugar in alcohol (DOMINO), approximately 2 kg for a footing of 500 cu.ft. (15 g per hl).

It is difficult to make a definite statement as to the average crystal size of this DOMINO icing sugar but according to samples of which the crystal size

has been estimated microscopically, this has been approximately 15–25 μ .

The crystal size at the end of the ripening period (see in Fig. 7/26) was approximately 0.06–0.09 mm. This would mean that the amount of crystallized sucrose at the end of the grain period would be approximately 3 kg of sucrose crystals per hl. of footing. This is still an extremely small crystal

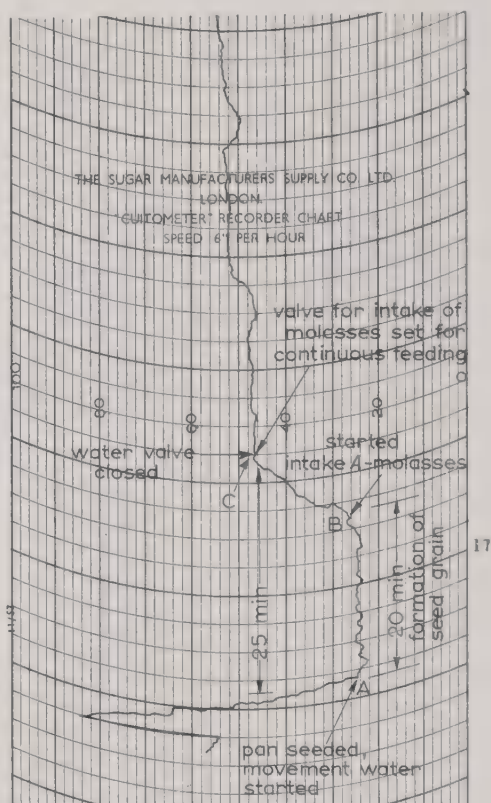


Fig. 7/26. Recorded conductivities in making a seed strike on A-molasses. Seed slurry introduced at A, at the same time admitted movement water. Amount of movement water is in balance with evaporation rate. Ripening of seed grain takes place at constant supersaturation. At B intake valve opened for A-molasses, at C valve for water closed.

content. It is recommendable to prolong the graining period with another 10 minutes till the crystal content of the footing increased to approximately 20% (20 kg of crystallized sucrose per hl) to be certain that there is only an extremely limited risk of false grain formation in the following phase of the boiling process.

In investigations on the technology of boiling, it is essential that special attention is given to the following points:

1. The method of making a uniform slurry of seed crystals to be used as starting material of the crystallization process in A-molasses.

2. A careful study of the recommended purity level of the *A*-molasses to have the shortest possible time for the ripening of the introduced seed with the prevention of the formation of conglomerates.

3. The time required for the ripening of introduced seed maintaining a good circulation in the pan by the introduction of movement water, and eventually reducing the vacuum on the pan with a corresponding increase of the temperature of the crystallizing molasses which will speed up the crystallization and shorten the time of ripening.

4. The exact determination of the end point of the growth of the seed grain in the footing, being certain that a sufficient amount of crystallized sucrose is present so that there is practically no risk for secondary grain formation in the second phase of the crystallization process.

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CHAPTER 8

DETERMINATION OF HEAT TRANSMISSION AS AN INDIRECT METHOD FOR THE DETERMINATION OF THE VISCOSITY AND SUPERSATURATION OF TECHNICAL SUGAR SOLUTIONS

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1. Introduction

The object of pan boiling is the production of a fine even crop of sugar crystals. A primary condition for the attainment of this end is the maintenance of a control over the rate of crystallization during growth. Basically a crystal surface maintained in a solution will only grow if the concentration of the solution is maintained at a level greater than the saturation concentration. Such a solution is said to be supersaturated.

A crystal surface in a supersaturated solution grows at constant rate provided the degree of supersaturation remains constant. Early studies of the kinetics of crystal growth showed that this rate was proportional to the degree of supersaturation (defined in Chapter 4)¹. McCABE² further found that the volumetric rate of growth was proportional to the crystal area. A crystallite maintained in a supersaturated solution initially adds in unit time a relatively small amount of sugar to itself but as the area increases so does the rate of growth.

Control of the rate of growth thus demands control of the degree of supersaturation. In some ways control of supersaturation is a relatively straight-forward process. Any increase in the rate of evaporation relative to the rate of crystallization will result in water being removed from the solution faster than sugar and thus produce an increase in the degree of supersaturation. Any addition of a saturated or undersaturated solution or even of water itself will lower the degree of supersaturation. Accordingly if we have some indication of the level of supersaturation reached at any stage in the boiling operation as well as an indication of the optimum level

for efficient performance, our course of action will be quite clear. Control of crystallization rate depends only on the measurement, direct or indirect, of the level of supersaturation.

While the level of supersaturation increases regularly with the concentration, direct measurement of concentration cannot be substituted for measurement of the degree of supersaturation for the reason that the saturation concentration varies regularly with the temperature and the degree of purity of the liquor. Fortunately the property of viscosity has been shown to be fairly closely connected with the measure of the degree of supersaturation; so that viscosity measurements, or measurement of physical properties closely allied to viscosity – such as heat transmission and electrical conductivity, can be used as indirect indicators for the degree of supersaturation.

2. Relation between Viscosity and Supersaturation

The viscosity of a sugar solution at any fixed concentration decreases rapidly with increasing temperature. The viscosity of a solution at fixed temperature increases rapidly with increase in concentration, particularly in the higher ranges of concentration. Finally at any fixed concentration the degree of supersaturation falls with rising temperature due to the increase in solubility with increase in temperature. As a net result if we take a solution at a fixed level of supersaturation and alter the temperature we get two opposing effects. Suppose the temperature is raised. The viscosity tends to fall on account of higher temperatures but at the same time tends to increase on account of the higher concentration required to maintain the same level of supersaturation at the higher temperature. As a net result the viscosity tends to change relatively little with temperature at a fixed level of supersaturation. MICHELI and DE GYULAY³ have published a series of curves for viscosity *vs.* temperature at a series of fixed levels of supersaturation. Some data obtained by these authorities are presented in Fig. 8/1. The curves shown are curves of viscosity *vs.* temperature. The full lines refer to conditions of constant concentrations and the broken lines to conditions of constant supersaturation. The first graph, which refers to data obtained from pure sucrose solutions, shows that the viscosity at constant supersaturation decreases somewhat with temperature but tends to become steady from temperature between 60° and 80° C. The other graphs which refer to mill materials of different purities show the viscosity – temperature curves attaining minimum values within the working range of temperature.

These curves mean, physically, that a measurement of the viscosity, or

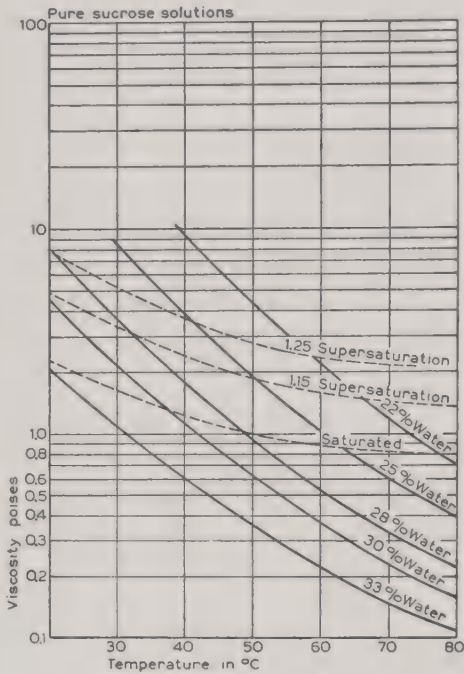


Fig. 8/1a. Relation between viscosity and supersaturation. Graph 1.

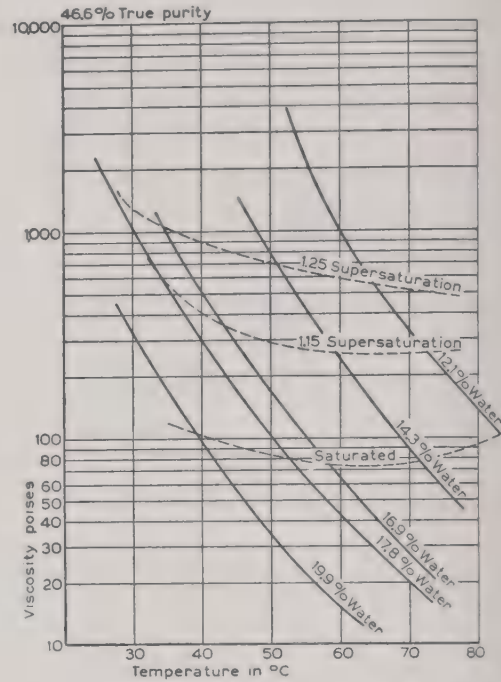


Fig. 8/1b. Relation between viscosity and supersaturation. Graph 2.

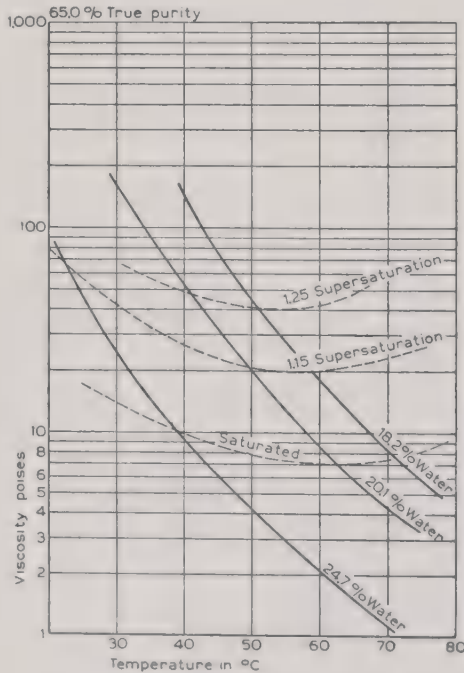


Fig. 8/1c. Relation between viscosity and supersaturation. Graph 3.

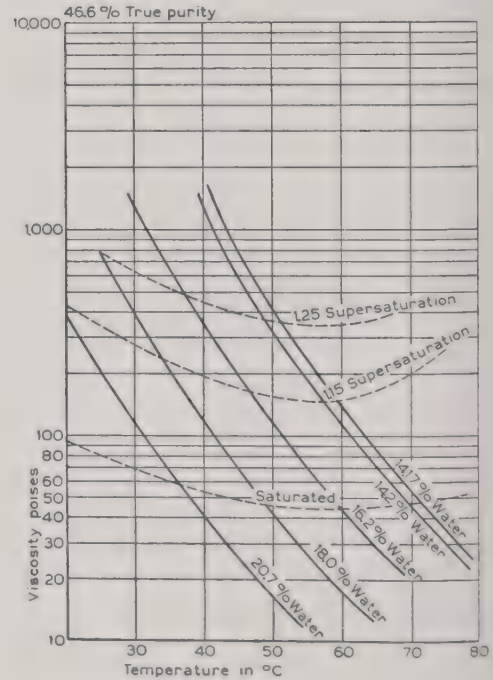


Fig. 8/1d. Relation between viscosity and supersaturation. Graph 4.

of any other property directly related to the viscosity, can be taken as a measure of the degree of supersaturation at any temperature within the range for which the curves are sensibly parallel to the temperature axis.

One of the most convenient indirect measures of viscosity is the electrical conductivity. The factor which determines the electrical conductivity of a liquid containing a given number of electrically charged ions is the speed with which these ions can move under the influence of the electrical force. This speed, in turn, is controlled by the frictional forces due to the viscosity of the liquid and thus, through the relationship of MICHELI and DE GYULAY*, by the degree of supersaturation. The technical exploitation of this relationship has been treated in Chapter 7. For the purposes of the present chapter, it is necessary only to point out that control by electrical conductivity is related to control by other indirect methods allied to viscosity and in particular to those methods which are dependent on measurements of heat transmission.

3. The Measurement of Heat Transmission

The overall heat transfer coefficient between a standard solid surface and the massecuite under test is a property which is relatively easily measured and is largely dominated by the viscosity of the massecuite and thus, in view of what has been said above, by the degree of supersaturation.

Before however we explore the relation between the degree of supersaturation and the heat transfer coefficient, some consideration must first be given to the practical measurement of, at least, the relative heat transfer coefficient under different operating conditions.

The heat transfer coefficient (*h*) is, it will be remembered, measured by the quantity of heat crossing unit area in unit time under an overall unit temperature difference, or

$$h = \frac{1}{A \Theta} \cdot \frac{dQ}{dt} \tag{1}$$

where

- $\frac{dQ}{dt}$ = rate of flow of heat
- A = the area
- Θ = temperature difference.

In instruments to measure or record *h*, heat is supplied to (or removed from) solid bodies of fixed dimensions and the temperature difference between the solid and fluid noted for a fixed rate of heat input. Alternatively

* The name of the second author has subsequently been changed by deed-poll to DULOX.

the heat input (positive or negative) could be adjusted to give a predetermined temperature difference. In either instance the heat transfer coefficient may be taken as proportional to the ratio:

$$\frac{\text{rate of heat input}}{\text{temperature difference between solid and fluid}}$$

In the transmission boiling recorder, described for example by TROMP⁴ a suitably located small copper vessel is heated by steam to a constant temperature and the rate of heat flow through the surface is proportional to rate at which steam condenses in the vessel. The condensate is drawn off through a trap and measured. The volume collected in unit time, corrected

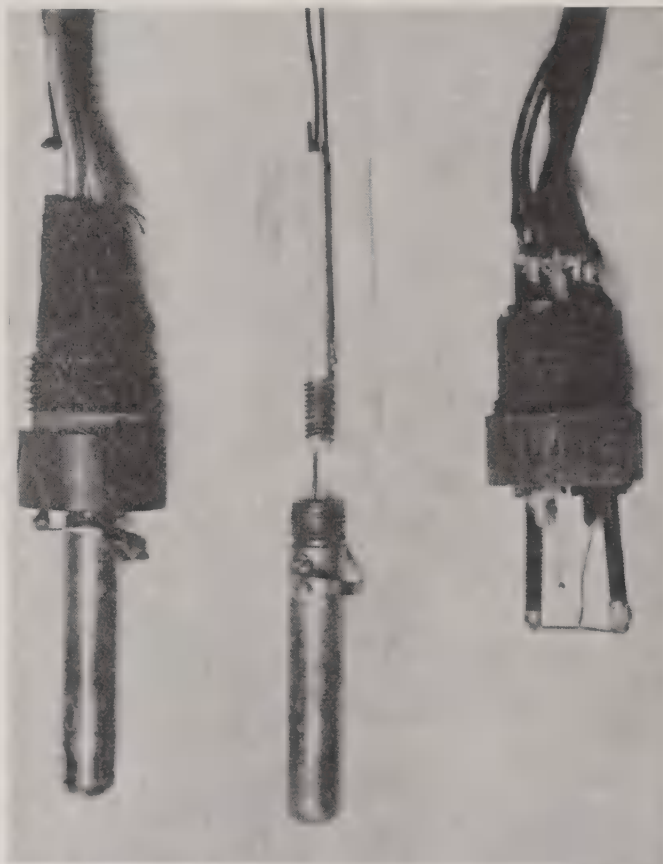


Fig. 8/2. Electrical instruments for measuring comparative heat transfer coefficients.

if necessary for any large change in the temperature of the masseccuite, is directly proportional to the heat transfer coefficient.

In a modification of this instrument described by DITMAR JANSSE⁵ the measuring vessel is cooled by a stream of cold water which enters at a constant temperature and at a constant flow rate. The heat flow, this time

from the liquid to the solid body, causes a rise in the temperature of the water circulating through the solid, and, since the flow rate of water is maintained constant, is directly proportional to that temperature rise.

A series of electrical instruments for measuring comparative heat transfer coefficients have been described by BOSWORTH and DULOV⁶. Two types of

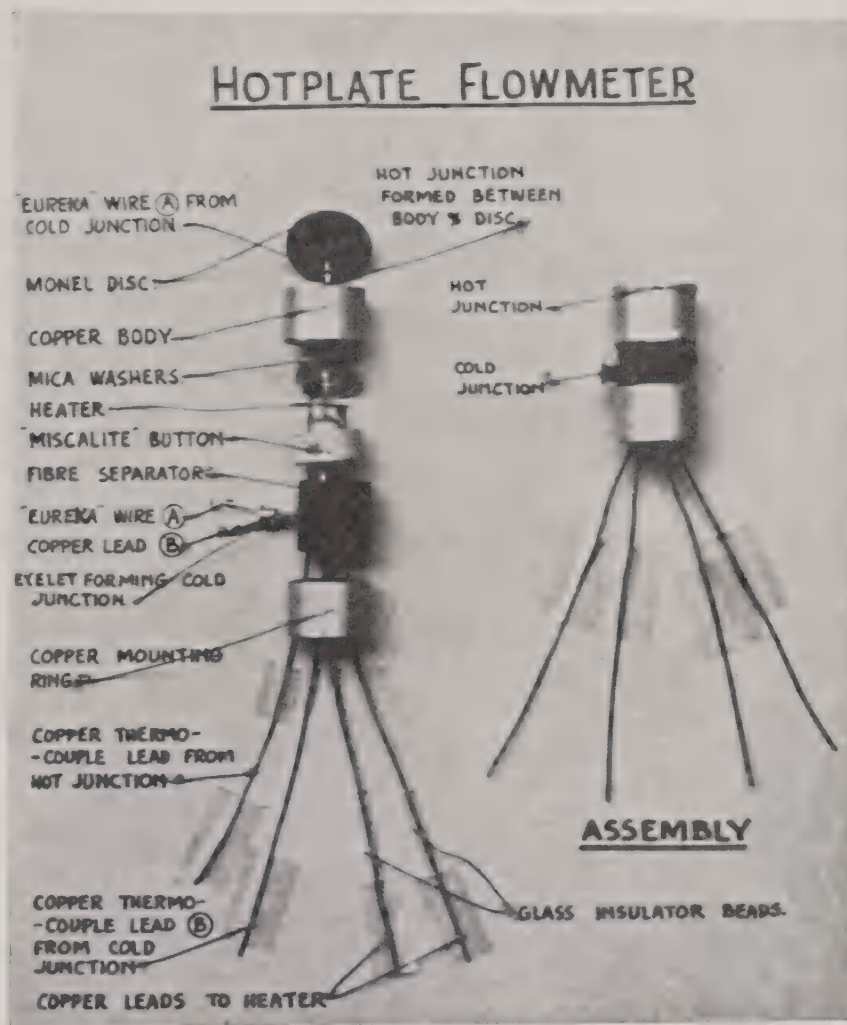


Fig. 8/3. Hotplate flowmeter.

these instruments are illustrated in Fig. 8/2, and a third in Fig. 8/3. The prototype is shown on the right hand side of Fig. 8/2.

The instrument is mounted on a formica plug which can be screwed into a 1" O.D. pipe for insertion in a vacuum pan. Four electrical leads pass through the formica plug. One pair carried electrical current for heating the short length (about 2 cm) of 23 S.W.G. nichrome V wire. Silver-

soldered (with a minimum amount of solder) at the centre of this wire is a small copper-constantan thermocouple of 32 S.W.G. wire. The first junction of this couple takes up the temperature of the electrically heated wire while the second junction, some 5 mm away and shown clearly in the photograph as a bead, takes up the temperature of fluid (or massecuite) in the vicinity of the wire. With the nichrome wire heated to any desired temperature by the passage of an electric current the thermocouple will give a reading proportional to θ , the temperature difference from solid to liquid.

The instrument shown on the left hand side of Fig. 8/2 (with exploded view in the centre) is an indirectly heated modification. The electrical heater is the small nichrome coil wound on a double-bored ceramic bead and shown in the central figure. This is normally pushed to the end of the hollow monel capsule, and electrically, but not thermally, insulated from it by the sheet of mica shown unrolled in the central figure. The hot junction is internally welded to the head of the capsule and the cold junction externally welded to its base as shown. The thermoelectric combination used is monel-copper which is not very different in its thermoelectric power from constantan-copper.

Fig. 8/3 gives in view and in detail, a more compact form of the indirectly heated instrument. In both forms the hot junction from which effectively the heat transfer coefficient is measured, is placed on the inside of the heated surface. This construction was adopted when it was found that any irregularity on the surface tended to catch fibres, bag-hairs etc. and so build up a mass of rather indefinite thermal properties.

4. Theory of the Electrical Instrument

Since the hot wire, or coil of the heater, is made of an alloy resistance wire, its resistance, to a first approximation, does not change with the temperature. Let R represent this resistance. When a current I flows through the heater the power dissipated, or heat generated per unit time, *i.e.* the dQ/dt of equation (1) is

$$I^2 R \text{ watts}$$

For any fixed instrument R may be taken as fixed. The heat generated per unit time and ultimately dissipated into the fluid surrounding the heated body is thus proportional to

$$I^2$$

Again the galvanometer deflection (G) is directly proportional to the tem-

perature difference θ . Consequently the required heat transfer coefficient is proportional to

$$I^2/G$$

Measurement of the heat transfer coefficient for a fluid of unknown properties may therefore be obtained with any instrument of the types described above by comparing the values of I^2/G with the values obtained in some standard liquid.

The ancillary equipment required for these measurements is particularly simple and consists in

- (1) a step down transformer giving about 32 volts A.C. output;
- (2) a series of barretter tubes with associated switching in order to control the current, if necessary over long periods, at a series of fixed values;
- (3) an A.C. ammeter (0–12 A scale) for measuring the heating current;
- (4) a sensitive galvanometer for measuring the small e.m.f.'s produced by the thermocouple.

A.C. current rather than D.C. current was found necessary for heating the hot wire instrument as otherwise any dissymmetry in the weld joining the thermocouple to the hot wire resulted in adding a spurious D.C. e.m.f. to the thermocouple circuit which changed sign when the heating current was reversed. In the indirectly heated instrument where the thermocouple circuit is electrically insulated from the heater circuit either A.C. or D.C. could be used for heating.

On account of their greater thermal capacity the indirectly heated type takes much longer to settle down to thermal equilibrium after either changing the heating current or the nature of the fluid in which the instrument is immersed. The directly heated wire on Fig. 8/2 attained thermal equilibrium in less than 20 seconds. The indirectly heated capsule took up to 10 minutes. For measurement in pan control the long delay period is a distinct advantage as it smoothed out random fluctuations due to the passage of bubbles over the measuring instrument.

5. Heat Transmission under Static Conditions

When a solid body in a quiescent fluid is subjected to heating or cooling; then so long as the former is not so intense as to cause boiling, or the latter so intense as to cause freezing, the rate of heat transfer may be obtained from the simple expression for natural convection. For long cylindrical bodies held horizontally in a fluid with as low a convective modulus as a mass of fluid this expression takes the form

$$\frac{hd}{k} = 0.49 (ad^3\theta)^{1/4} \quad (2)$$

where

- a = convective modulus of the fluid
- k = its thermal conductivity
- d = diameter of the solid body
- θ = temperature difference.

The quantity a in turn may be expressed in terms of better known properties

$$a = \frac{c_p \cdot \rho^2 g \beta}{\eta k} \quad (3)$$

where

- c_p = specific heat at constant pressure
- ρ = density
- β = coefficient of cubic expansion
- η = viscosity
- g = acceleration due to gravity.

On substituting equation (3) in (2) we get

$$h = 0.49(d^{-1/4} k^{3/4} \rho^{1/2} c_p^{1/4} g^{1/4} \beta^{1/4} \eta^{-1/4}) \theta^{1/4}$$

and this is the factor which will be proportional to the I^2/G in the electrical instrument discussed in the sections above.

It will be noted first of all that h increases slowly with θ so that measurement of heat transmission in quiescent fluid should strictly only be taken at comparable values of θ .

Apart from its dependence on θ and d the heat transfer coefficient also varies with the properties k , ρ , c_p , β , and η each of which is influenced by the degree of supersaturation and, possibly independently, by the temperature and the purity. It is possible, however, to simplify the problem by taking into account known relationships between these properties.

For example the coefficient of cubic expansion (β) may be expressed as

$$\beta = \frac{1}{\rho} \frac{d\rho}{dT}$$

The $\frac{d\rho}{dT}$ or the change in density with change in temperature at constant composition may, for sucrose solutions, be read off from tables of temperature correction to brix reading and is, for temperatures and densities in which we are interested, practically independent of the concentration and thus independent of the degree of supersaturation.

By elimination of the constant factors from equation (4) we then get

$$h \propto (k^{3/4} \rho^{1/4} c_p^{1/4} \eta^{-1/4}) \theta^{1/4}$$

The thermometric conductivity, or thermal diffusivity ($k/c_p\rho$) has been shown to be a property which has practically the same value for all liquids (BOSWORTH⁷) and is not therefore expected to vary with the brix of a sugar solution. We are thus left with the variation for h

$$h \propto k/\eta^{1/4}$$

The thermal conductivity k changes relatively little with the composition although there is some evidence that k passes a minimal value at the saturation concentration. The dominating factor in determining the heat transfer coefficient under these conditions is however the viscosity η . Control of supersaturation by means of a measurement of h is thus in effect a control on a viscosity measurement. Further, since h is proportional to the inverse fourth root of the viscosity, control in terms of static heat transfer is a relatively insensitive one compared with say control in terms of electrical conductivity which, roughly, is inversely proportional to the viscosity and not to its fourth root.

6. Heat Transmission under Dynamic Conditions

When the heat transmission recorder or other equivalent instrument is used as an effective control of the degree of supersaturation it is not placed in stagnant pockets of liquid but more commonly in the open circulating fluid. For such systems the appropriate expressions are those for heat transmission under the influence of forced and not of natural convection.

For a liquid flowing with velocity v past a heated cylindrical body the expression usually given for the heat transfer coefficient becomes:

$$\frac{hd}{k} \cdot \left(\frac{k}{c_p\eta} \right)^{0.3} = 0.35 + 0.47 \left(\frac{d\rho v}{\eta} \right)^{0.52} \quad (5)$$

See also MCADAMS⁸.

When the degree of supersaturation and thus the brix is changed, both the viscosity η and the Prandtl number $\left(\frac{c_p\eta}{k} \right)$ are changed. For a given increase in brix the relative increase in the viscosity and in the Prandtl number are practically equivalent since k/c_p changes only slightly with the composition. An approximate expression for the change in the heat transfer coefficient then reads

$$h = A\eta^{0.3} + Bv^{0.52}/\eta^{0.22} \quad (6)$$

where A and B are constants for any particular type of hot body and masse-cuite.

The first term in equation (6) thus increases with increasing concentration while the second term decreases with increasing concentration but increases with increasing velocity. As a nett result therefore the change in h produced by decreasing concentration is not a particularly sensitive or accurate measure of the change in viscosity and thus change in supersaturation. *The measurement of h is, on the other hand, quite a sensitive measure of the change in the velocity of flow (v) of the fluid past the measuring device. The heat transmission recorded on the hot wire or the hot capsule device used under dynamic conditions is neither a sensitive nor a reliable measure of the degree of supersaturation or of any related property except in as much as the circulating velocity v can be made dependent on the property to be measured and controlled. Indeed as will be shown in succeeding sections this is precisely the way in which instruments of this nature are employed. For the moment, however, we will divert to consider the relation between heat transmission, viscosity and the velocity of circulation.*

7. Relation between Viscosity and Velocity of Circulation

This subject has been studied in the laboratory by means of equipment outlined in Fig. 8/4. The lower element A consists in a hot wire thermocouple device of the same type as that shown in Fig. 8/2. This was immersed in a thermostatically controlled $1\frac{1}{2}$ " diameter test tube of the liquid under test. At various distances from 5 mm to 5 cm above A and parallel to it was placed a simple thermocouple element B .

An experiment was commenced by switching on a predetermined heating current to the hot wire of element A . The e.m.f. of the thermocouple attached to A immediately began to rise and passed a peak value usually in less than a minute. The reading of the thermocouple B , however, remained zero for a time often of several minutes and then commenced to rise and again passed a maximum as the hot stream generated by the heating of A reached the point B . The various curves shown in Fig. 8/5

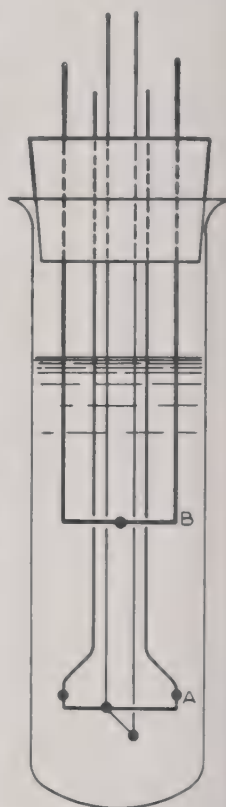


Fig. 8/4.
Apparatus for
studying speed
on convection
currents.

show the variation in the delay to the response of thermocouple *B* with different qualities of material and temperatures of heating the wire *A*.

The time lapse between the attainment of the peak in the e.m.f. from thermocouple *A* and that from thermocouple *B* is a measure of the time taken for the convection current to travel from *A* to *B* and thus of the velocity of the convection current.

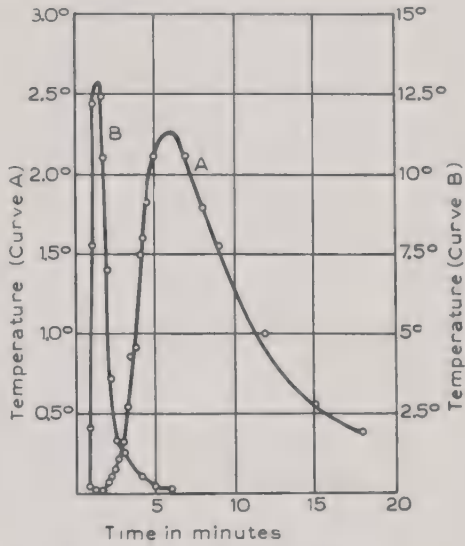
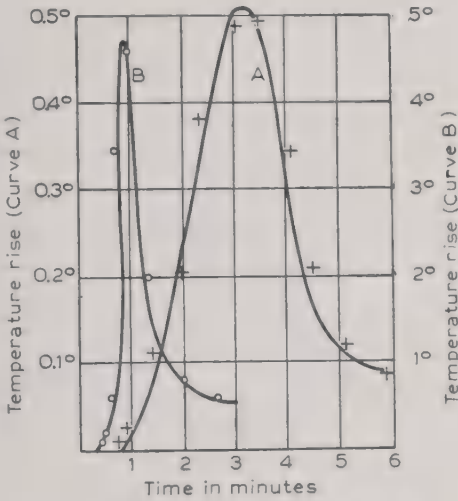


Fig. 8/5. Relation between viscosity and velocity of circulation.

Fig. 8/6. Relation between viscosity and velocity of circulation in higher density material.

The velocity of the convection current was measured with this apparatus at a series of different rates of heat input to the wire *A* and in syrups of different concentrations and purities. The most important factors controlling the velocity of circulation proved to be the temperature θ to which the wire *A* was heated in excess of that of its surroundings and the viscosity (η) of those surroundings. A long series of experiments gave as a net result

$$v \propto \theta \eta^{-0.15}$$

Since the primary heat flow from the wire *A* to the surroundings is roughly proportional to $\theta^{\frac{1}{2}}$ we may conclude that the intensity of the convection current increases more than proportionally to the intensity of the heat transmission (being roughly proportional to h) and decreases not quite proportionally to the inverse of the viscosity.

We conclude therefore that if fixed surfaces supplying heat to the masse-cuite are in existence then the intensity of the convection currents set up under standardised conditions is an inverse measure of the viscosity of the masse-cuite and thus, indirectly, of its degree of supersaturation.

8. The Heat Transmission Recorder

This instrument which has already been mentioned in the sections above consists of a copper vessel which is placed in the well of the pan well below the graining level and is connected by copper tubes to the pan wall and to the pan bottom. Steam is supplied through a needle valve. When the heat transfer coefficient at the surface of the copper vessel is high, rapid condensation occurs in the vessel and the steam cannot escape through the needle valve sufficiently rapidly to maintain the pressure. This pressure therefore drops and the steam condenses at a lower temperature. A thermometer placed in the condensate and connected to a recorder gives a record of this temperature. The recorder simultaneously maintains a record of the vacuum at the top of the pan. This pressure is, of course, an indirect measure of the temperature of the massecuite around the copper vessel while the temperature of the condensate is an indirect measure of the rate of condensation and thus of the rate of heat flow to the massecuite from the steam at condensate temperature. From the two records the heat transfer coefficient may thus be derived.

In concordance with the relations which have already been discussed, the heat transfer coefficient, although to some extent influenced by the viscosity of the massecuite in which the control vessel is situated, is much more strongly influenced by the rate of flow over the vessel.

Again the rate of flow of the massecuite over the heating coils is strongly influenced by the viscosity of the massecuite at these coils. Consequently we find that the reading of the heat transmission recorder is predominantly influenced by the viscosity of the massecuite at the heating coils (and so by its supersaturation) *provided the velocity of flow over the controller is either the same as, or else directly proportional to, the flow rate over the coils.* For this reason the position of the controller in the pan is important. DITMAR JANSSE³ has discussed this matter. According to him the vessel to which the heat transfer coefficient is measured should be oriented vertically and placed in the centre of the downtake, well away from the walls or any feed pipes which might locally disturb the circulation pattern. The vessel should neither be placed in the lowest part of the downtake which in certain pans and under certain conditions is avoided by the circulation current.

Various extraneous factors which can influence the heat transfer coefficients and thus adversely affect the accuracy of estimates of the degree of supersaturation drawn from reading of the heat transmission have also been discussed by DITMAR JANSSE⁹. He lists the following:

(a) A high calcium content can produce abnormally high viscosity in the mother liquor of range 76–80° B. This lowers the heat transfer coefficient.

(b) The return of a larger proportion of nonsugar with poorly purged C-sugar can have the same effect as an abnormal calcium content.

(c) Improper attention to cleanliness in the effects can produce viscous polysaccharide material through bacteriological contamination.

(d) Unsuitable operating conditions as well as poor construction and high supersaturation can give abnormally low circulation rate in the pan and thus a low reading of the heat transmission recorder.

In a subsequent article, DITMAR JANSSE⁵ also refers to the necessity for cleanliness within the vessel of the heat transmission recorder itself. In the low temperature instrument – supplied with cold water and not steam – it is desirable to filter the water to avoid the build up of thermally resistant films on the inside of the vessel.

GONZALEZ MAIZ¹⁰ has reported on experience with the DITMAR JANSSE pan control apparatus. He claimed that the control graph of this instrument registered every variation, no matter how small, in the factors influencing the state of concentration within the pan, and concluded that this instrument was 'the most perfect of all' so far proposed for the control of pan operation.

SOESMAN¹¹ has compared the performance of a number of pan control instruments, among them the heat transmission recorder. He pointed out in particular that this method is theoretically not preferable to the conductivity method (the relation between supersaturation and heat transmission is less direct than the relation between electrolyte conductivity and supersaturation.) He further claimed that either technique provides a method of control which is independent of variation in pressure but noted that the effect of purity changes on the relation between the control property and the degree of supersaturation required close investigation. This statement still holds true to-day.

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CHAPTER 9

TECHNOLOGY OF SUGAR CRYSTALLIZATION

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1. Introduction

The manufacture of sugar for human consumption has been characterized from time immemorial by the transformation of the collected juice of sugar-bearing plants, after some kind of purification of the juice, to a concentrated solid or semi solid product that could be packed, kept in containers and which had a high degree of keepability.

The main characteristic in the history of the technology of sugar manufacture is that a raw material high in sugar being extremely susceptible to fermentation and decomposition is transformed via a concentration process to a preservable end-product which has maintained the main quality of the valuable ingredient, the sugar, its sweetness.

The history of the development of sugar manufacture has been described in an excellent way in two handbooks which should be a part of the personal library of every sugar technologist: VON LIPPMANN'S *Geschichte des Zuckers* (Julius Springer, Berlin, 1929) and NOEL DEERR'S *The History of Sugar* (Chapman and Hall, London, 1949).

The great developments in sugar manufacture come through the introduction of labor and time saving equipment in the processing technique; namely, the centrifugal and the vacuum pan. Today, in the world production of sugar, a distinction is made between centrifugal sugars and non-centrifugal sugars. The non-centrifugal sugars are still made as it has been done for hundred of years, by simply concentrating the purified juice in open pans to a solidified end-product.

Of the total world production of sugar (43 million metric tons) all the beetsugar (15 million tons) that is made today is centrifugal sugar. There have been some endeavors to manufacture from sugarbeets a sugar product containing all the nonsugars in the purified juices. This product was known

under the French name of 'sucre complet'. Today this endeavor is only of historical interest.

Of the total canesugar production of approximately 28–30 million metric tons per year, still a 7 to 8 million tons are made as a sugar product without the use of centrifugals to separate a large part of the nonsugars or impurities in the form of molasses. These sugars are known as *gur* in India, *panella* in Latin American countries, and under different other names varying from country to country but all characterized by the same principles of manufacture.

The art of sugar boiling to manufacture this kind of primitive sugars can, of course, be qualified as technology but it is not technology in the modern meaning of this word. The sugar boiler has a certain skill knowing how he must heat and evaporate the juices, which type of pan gives the best product as to consistency and color, and how he must determine the end-point in this concentration process. This all is more an art but we are justified in saying that modern or scientific principles are applied or involved.

This type of sugar making is open for scientific investigations thereby enabling us to study the causes of variations in the quality of the end-product, whereby the meaning of the word quality is determined by the taste, customs and tradition of the consumers. It has for instance been found that to make a hard *gur* it is necessary that the purity of the juices to be concentrated does not surpass a certain percentage of reducing sugars. Otherwise the end-product is soft and wet, and not of an appearance that it is favored by the customers.

The color of the sugar is affected by the system of boiling, the construction material of the pans, the quality of the cane, and a number of other factors partly unknown. Considerable variations in the quality and in the evaluation of the end-product occur at all places where sugar is manufactured.

We are not going to consider this type of sugar making in particular. Our interest is in the development of the modern sugar production as centrifugal sugars.

The end-product that reaches the consumer is for beetsugar always white sugar. This is made either directly from beet juices after raw juice has been purified by the carbonation process with a partly recrystallization of some of the products in the beetsugar factory, or it is made as a raw sugar practically never consumed directly, but sent to the refinery where this raw sugar is transformed into a white sugar product of a high purity. This sugar is usually called refined sugar. There is not always made a distinction in the sugar trade between a refined sugar and a white sugar made directly

by beet factories. In many cases there is neither from a chemical or physical point of view a justification for making this distinction. The chemical composition of these two types of sugar is practically identical and in their physical appearance they are in many cases indistinguishable.

With canesugar a difference is always made between plantation white sugar made directly from the cane juices, after the juices have been purified in a special way (sulfitation, carbonation, middle juice carbonation), and refined canesugar. The chemical composition of these two types of sugar is in broad lines noticeable. A plantation white sugar is crystallized from boilings with a purity between 80 and 90. The resulting sugar has a certain amount of nonsugar impurities (reducing sugars and ash) usually higher than found in similar products as made by refineries.

The differences in the sugars as made by canesugar factories are primarily a distinction in products resulting from:

- (a) raw sugar factories,
- (b) plantation or direct white sugar factories,
- (c) raw sugar mills combined with a refinery as one operating unit.

The system of crystallization in raw sugar factories and plantation white sugar factories is identical. Differences, as far as they exist, refer to the average grain size of the manufactured end-product. *Raw sugar* today, as we were able to examine the quality characteristics of sugars produced in different countries and different mills, refers mainly to the average grain size and the uniformity of the grain size. The sugar is usually distributed, when it is a direct consumption sugar, as granulated sugar consisting of dry sugar crystals, free of lumps, composed of individual crystals mixed with a certain amount usually inevitable twin crystals and conglomerates. It is a dry sugar having an average grain size between 0.3 to 1 mm linear.

The trade distinguishes the different types of grain size by expressions as: finest granulated, fine granulated, standard granulated, coarse granulated, and sometimes by specific words as: NIVAS crystals, being an extra coarse sugar which was manufactured in Java with the destination of the Persian Gulf's ports and ports of the China mainland.

When finer grades of sugar are made they are usually not manufactured as a dry sugar, but are mixed with a certain amount of invert sugar syrup and are then called *soft sugars*. These sugars, consumed particularly in China and Japan, can be made either as plantation white sugars or they are made in refineries from raw cane sugars. The average grain size of this type of soft sugars is 0.1 to 0.2 mm linear. When these sugars are made from low purity products they are usually called *brown soft sugars* or *molasses sugars* containing a certain percentage of the original mother liquor, being a

molasses of low purity retained by the sugar in the centrifugal process to eliminate the larger part of the surrounding molasses in the original massecuite.

The tendency exists today that for industrial applications of sugar in the highly developed countries the sugar is no longer delivered as a crystalline product, but is delivered directly to the user as a concentrated solution either as a solution of pure sucrose or consisting of a mixture of sucrose and invert sugar. This product is called *liquid sugar* and it is partly made in special refineries with a purity surpassing even the highest standards of granulated refined sugars. This product is becoming more and more important. In a highly industrialized country as the U.S.A. the delivery of liquid sugar to refineries has surpassed the 1 million tons annually in 1956.

In the crystallization of sugar we are always dealing with a number of technical terms not absolutely standardized over the whole world; however, in the English-speaking countries with a certain uniformity we know exactly what is understood by these terms. The most common expressions in sugar crystallization are the following:

Syrup. This is a product resulting from the concentration of purified juices via evaporation of the excess of water in multiple evaporator effects. The syrup can be sulfured syrup, when a small amount of SO_2 has been added to the evaporator syrup, or filtered syrup, when it has been filtered over filter cloth with the addition of a certain quantity of filter aid or decolorizing carbon.

Liquor. This is usually called the purified and filtered solution of sugar, mostly resulting from dissolving affined raw sugars. It is used in refineries for the crystallization of the refined sugars.

Molasses is in most of the English publications on sugar technology called the mother liquor in a crystallized fillmass removed by centrifugation. It is distinguished in: first molasses, when it originates from the first boilings of the highest purity in the crystallization process; second molasses from second boilings.

Final molasses or *black strap molasses* is called the product eliminated from the manufacturing process of which no more crystallized sugar can be recovered by practical means.

In the crystallization process we distinguish the following words:

Massecuite written in English usually 'mass cuite', although it is originally a French word written 'masse cuite', which has been taken over literally in Spanish as 'masa cocida'. Synonymous with this word is *fillmass*, which originates from the German word 'Füllmasse'. Also an expression used many times in publications is simply the word *boiling*, which can be distinguished in: refined boiling, first boiling, second boiling, etc.

Skip was originally the transfer of a granulated boiling from one pan to another. Today it is used for the transferred volume of a boiling from one pan to another pan, from a pan to a seed crystallizer, or from a pan to the crystallizer.

To granulate is the expression for the crystallization process in which the sugar from a state of solution is transformed into sugar crystals or grain. The word 'granulation' for the crystallization of sugar is seldom used in technical publication.

Granulated sugar is all sugar delivered in the form of small crystals or grain. When the size of the grain surpasses a linear dimension of 1.5 mm, it is usually referred to as *sugar crystals* as, for instance, *Demarara crystals* and *coffee crystals*. When sugar is crystallized to still a larger size of the individual crystals, larger than 10 mm linear, it is called *candy*.

Run off is the mother liquor removed from a mixture of crystals and mother liquor by the centrifugal process. According to the type of boiling we distinguish: first run off and second run off. For refined sugar boilings it is customary to use for the mother liquor from the first refined sugar boiling the expression first run off. It is also customary to use for the word boiling or fillmass the expression *strike*.

In the centrifugal process, where the sugar is washed by steam or water or a combination of both, when the run off resulting from the washing process is separated from the mother liquor, a distinction is made in the separated mother liquor by calling it *green molasses* or *green run off*. The sugar solution resulting from the washing process is called *white molasses* or *white run off*.

In the execution of the crystallization process in vacuum pans we distinguish the different phases of the boiling process by the following terms:

Graining or *nucleation* or *seeding of the footing*. This is the formation of the nuclei or the introduction of fine crystals as nuclei to be developed during the crystallization process to sugar crystals of the desired size.

Ripening or *closing of the footing* which is called the development of the nuclei to such a size that a sufficient amount of crystal area per unit of volume is present that the crystallization can be continued at full rate without the practical danger of formation of nuclei or what they call *secondary grain* or *false grain*.

Cutting of the boiling is dividing the pan content over two or more pans, or storing a part of the massecuite in special storage equipment what is usually called the *seed crystallizer*.

Feeding of the pan is the introduction in a pan during the crystallization process of the raw materials (liquor, syrup or molasses) which must be crystallized.

Charge of a pan is called the volume of massecuite that is boiled in one pan unit and is usually expressed in cubic feet or hectoliters. A charge of a pan is also called the *net pan volume*.

All these words and expressions are used in the following review alternately. There is no special preference for any word or term. The use of these terms is to a certain extent a matter of local tradition, although the literal translation of these terms from one language into the other can be occasionally somewhat confusing. For example, in Dutch the first molasses in a raw sugar mill is called 'eerste afloop' or 'eerste afloopstroop', which should be translated by first run off syrup. This undoubtedly creates for English-speaking technologists some difficulties in understanding what is actually meant by these terms.

2. The Technology of Crystallization of Granulated Sugars

The following review discusses the crystallization of raw sugars, refined sugars and the afterproduct sugars in raw sugar mills and refineries. The modern technology of sugar manufacture as applied today for approximately 40 million tons of sugar annually is using for the crystallization process an apparatus that is called a vacuum pan or sugar pan. The fundamental characteristics are that in this equipment the sugar solutions to be crystallized are concentrated via evaporation under vacuum using steam or vapor introduced in specially designed heating elements in the form of coils or calandria. The concentration of the raw material varies from 60 to 70% dry solids or brix. The final concentration of the boiling contains between 8 and 14% of water depending on the type of boiling to be made and the quality of sugar to be delivered as a commercial product or to be used for reprocessing, corresponding with a brix varying from 90–105.

The crystallization process has three different phases, all requiring their own technique and operational conditions to obtain the highest efficiency and best results. These phases are :

- (1) the graining or nucleation,
- (2) the growth of the sugar crystals to the required crystal size,
- (3) the tying up or final concentration of the boiling to obtain the highest yield of crystallized sugar per 100 sugar in raw material.

In all crystallization processes it is ideal to obtain the crystallized sugar in the form of individual crystals of the most regular size and form. Experience has demonstrated that it is sometimes impossible to get uniform single crystals but that a large number of twin crystals are formed as a result of the presence of certain types of nonsugars or a high concentration of

certain types of nonsugars in the raw materials. All deviations from uniformity in crystal form must be qualified as undesirable.

A large percentage of twin crystals in a sugar has as a result that the volume weight of the final sugar is smaller than of absolutely uniform single crystals. In factories where the packing of sugar is done in uniform weight units these abnormalities can have considerable consequences and affect the economy of sugar production.

The presence of conglomerates must be avoided under all conditions because it is impossible to manufacture a sugar of a high degree of purity when the sugar contains a high percentage of conglomerates where a part of the mother liquor is included in these complex crystals which cannot be removed by a centrifugal or a washing process.

The tendency in sugar crystallization is that the graining or nucleation of a pan is done more and more via the introduction of a certain amount of extremely finely powdered sugar suspended in an organic liquid having no solubility for sucrose. The Java sugar industry introduced gasoline as the suspension liquid. GILLET of the Crocket Refinery introduced isopropylalcohol. It is a matter of availability and to a certain extent of tradition and personal preference which kind of organic liquid is used. A number of liquids can be used, if the boiling point of the liquid under the conditions of the crystallization process is lower than that of the pan content in which this seed or nuclei slurry must be introduced, and if it has no solubility for sucrose which causes a recrystallization of the finely powdered sugar or fondant sugar introducing an uncertain element in the dosage of the amount of seed sugar to be used.

It is customary that if a coarse sugar crystal is being made, a finer type of sugar resulting from the centrifugation of another type of boiling is introduced as seed. This sugar, for instance in raw sugar mills, can consist of the fine grained afterproduct sugars mixed with syrup to a magma and introduced in the pans for the commercial boilings as footing. This technique of crystallization is the simplest technique and is used in all sugar producing areas. The results obtained in the different factories are primarily a result of the availability of the proper equipment as correct and well balanced capacities of the different types of pan, containers, pipe connections and all that is concerned with the creation of operational conditions which according to our present knowledge results in a satisfactory performance.

3. The Aims of Sugar Crystallization

The aim of the crystallization of sucrose is twofold. Primarily, the sugar in solution must be transformed into a crystalline state that in the following step of sugar manufacture, the centrifugation, the highest possible yield of commercial sugar be obtained as a commercial product. Secondly, it is necessary that the amount of sucrose present in the raw material is transformed in the highest possible percentage into crystals, and that the final end-product of the crystallization process, the last mother liquor or black strap, is well exhausted.

We are dealing in the crystallization process with two types of efficiency. The first one is to obtain from the commercial boilings the highest possible recovery and a minimum number of crystallization steps to commercial end-product. The second one is that in the last or final boilings the by-product of sugar manufacture, the molasses, is liquidated with a minimum amount of recoverable sugar, since every part of sugar present in the molasses which can be crystallized is an economic loss.

In the manufacture of raw sugar it is customary today, in 80% of the canesugar factories, that the last product sugar is returned to the pan floor as seed for the commercial boilings. In the manufacture of plantation white sugar this system is not recommendable because the sucrose crystallized from mother liquor with a low purity (< 60) always contains a certain amount of nonsugars included, occluded or syncrystallized with the sucrose which affects the purity of the final product.

In white sugar factories it is customary to dissolve the last product sugars, usually after affination, and to return the remelt eventually after filtration to the syrup for recrystallization. The sugar from an intermediate boiling is used in this case as nucleus for the commercial boilings.

4. Desugaring of Boilings and Nonsugar Circulation

The ideal is to crystallize the sugar starting with the raw material, the syrup, in a minimum number of boilings of descending purity, to final molasses. The most common practice today is, in canesugar factories with a syrup purity between 82 and 88, to crystallize the sugar in three different boilings. The first two boilings deliver the commercial product. The last product boiling is for the maximum desugaring or exhaustion of the final molasses.

With modern equipment, particularly the introduction of crystallizers with cooling or heat exchange elements, it is possible in raw sugar mills to have a complete desugaring from syrup to molasses in a 2-boiling

scheme. This represents tremendous progress from a technological point of view. The commercial product is made from one type of boiling and can be absolutely uniform, which becomes more and more necessary with the introduction of modern centrifugals which are practically automatically operated, which can be done only with satisfactory results if the material

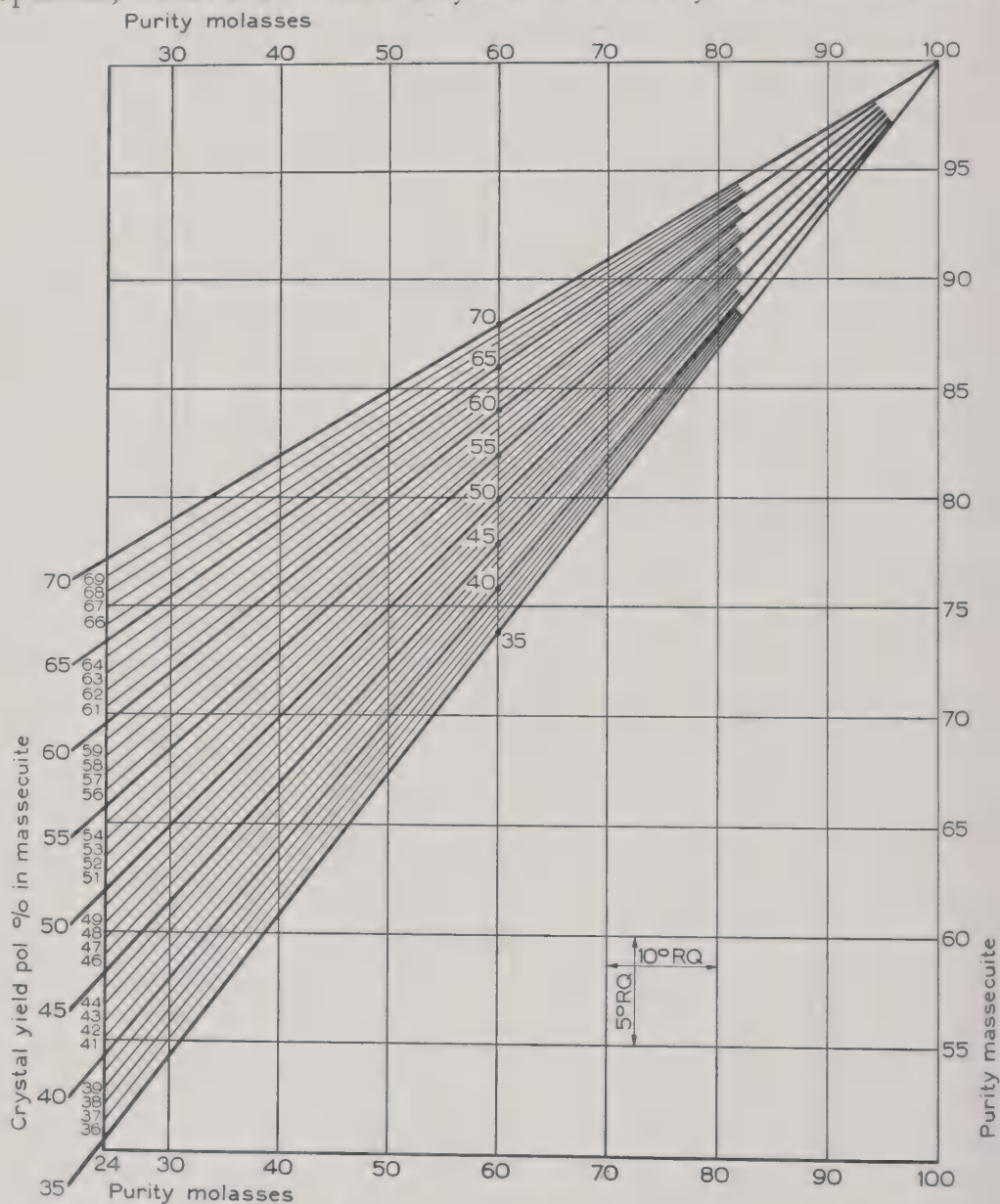


Fig. 9/1. Relation between purity massecuite and purity molasses for the determination of crystal yield % pol in massecuite for massecuite purities between 50 and 100 and molasses purities between 20 and 100.

to be subjected to centrifugation is uniform and does not change from hour to hour or from boiling to boiling.

The most important figure in judging the performance of a crystallization process is the desugaration or the amount of sucrose obtained in crystallized form per 100 sucrose in the boiling, respectively raw material to be boiled. The calculation of this yield of recovered sugar is usually done via the NOEL DEERR S.J.M. formula or what was known before the S.J.M. formula was adopted generally in the cane sugar industry as the HULLA-SUCHOMEL formula. This formula is usually written as follows:

$$\text{crystal \% on brix in massecuite} = 100 \frac{\text{purity massecuite} - \text{purity molasses}}{100 - \text{purity molasses}}$$

or

$$\text{crystal \% pol in massecuite} = 100 \frac{\text{purity massecuite} - \text{purity molasses}}{\text{purity massecuite} (100 - \text{purity molasses})}$$

This formula can be represented in a graph (Fig. 9/1.)

The desugaration or the calculated crystal yield must be a part of the standard technical control of all factories with an interest in the efficiency of the pan station. In Fig. 9/1, the crystal yield has been calculated for all types of boilings as met in sugar factories between 50 and 100 purity and with molasses or run off purities between 20 and 100.

It is practical for a sugar laboratory to construct detailed monograms for the customary types of boiling which can be made in very great detail and deliver directly the crystal yield without any calculation.

In Fig. 9/2 a graph is reproduced for *A*-strikes or first massecuites in plantation white sugar factories with a purity range for the boilings between 85 and 94.5, and with corresponding molasses purities between 50 and 90. For the very high purities of boilings as used in refineries, this method of calculation of the crystal yield via purities is not accurate enough because the accuracy of the determination of the purity surpasses the normal variations in the calculated crystal yield. Here, different methods must be used based for instance on the conductivity determination under standardized conditions (for example 5 brix solutions at 27.5 °C) and to introduce instead of the purity the pol-conductivity ratio for boiling and run off, and to calculate by the same formula the crystal yield:

$$\text{crystal yield \% sugar in massecuite} = 100 \frac{\frac{\text{pol}}{\text{conductivity}} \text{ massecuite} - \frac{\text{pol}}{\text{conductivity}} \text{ run off}}{\text{pol/conductivity massecuite}}$$

The present crystallization technique is that for the high purity boilings for the commercial product practically the total crystallization takes place in the vacuum pan. The crystallizer between vacuum pan and centrifugal

acts merely as a storage reservoir for the massecuite but does not assist substantially to increase the amount of recovered crystallized sugar.

In a few countries a technique has been developed to use the crystallizer station not only as a piece of storage equipment, but as actual additional equipment for crystallization. This must be done by cooling using the

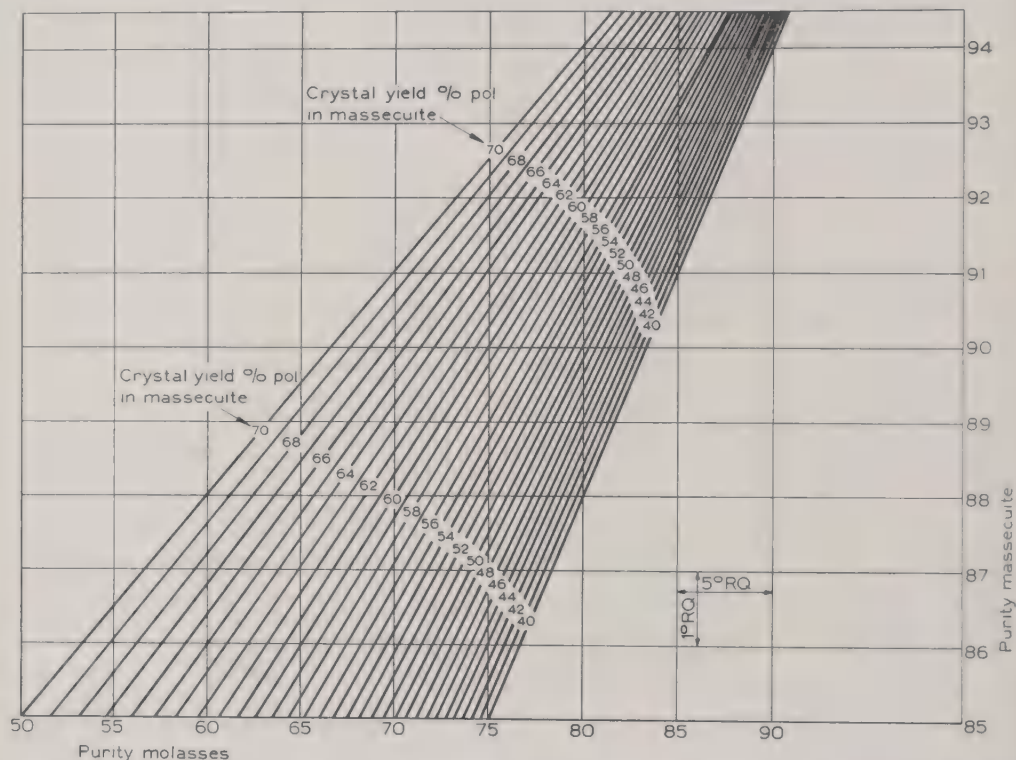
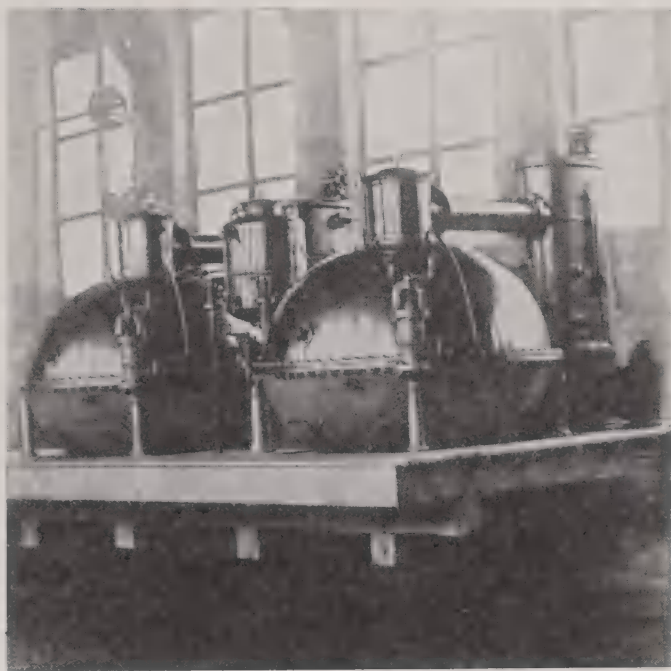


Fig. 9/2. Relation between purity massecuite and purity molasses and crystal yield % pol in massecuite for massecuite purities between 85 and 94.5 and molasses purities between 50 and 90.

decrease in solubility of sucrose at lower temperatures as an additional step for realizing the highest yield of sugar as granulated product from raw material to centrifuged sugar.

The 3-boiling scheme, with a consequent maximum desugaring in the first two boilings and the use of the *C*-sugar as seed for the commercial boilings, was introduced systematically in Java around 1910. This system was named after the technologist who introduced this system for the first time, the PASMA system. This system made necessary the introduction of a special crystallizer or storage tank for the *C*-sugar mixed with syrup to be used as footing for the commercial boilings. This piece of equipment, built usually at the highest floor in the sugar mill above the level of the pan floor, was given the appropriate name of zeppelin. Although we realize

that this system of boiling was a tremendous step forward, we must state that today a large number of factories, even starting with a syrup purity of 82 to 85, are applying a 4-boiling system and even occasionally a 5-boiling system which is not only confusing for the outsider but must be confusing for the insider.



Courtesy Stork-Werkspoor

Fig. 9/3. VAN VLISSINGEN pan as introduced in the sugar industry in the first part of the 19th century, constructed according to the principles of HOWARD.

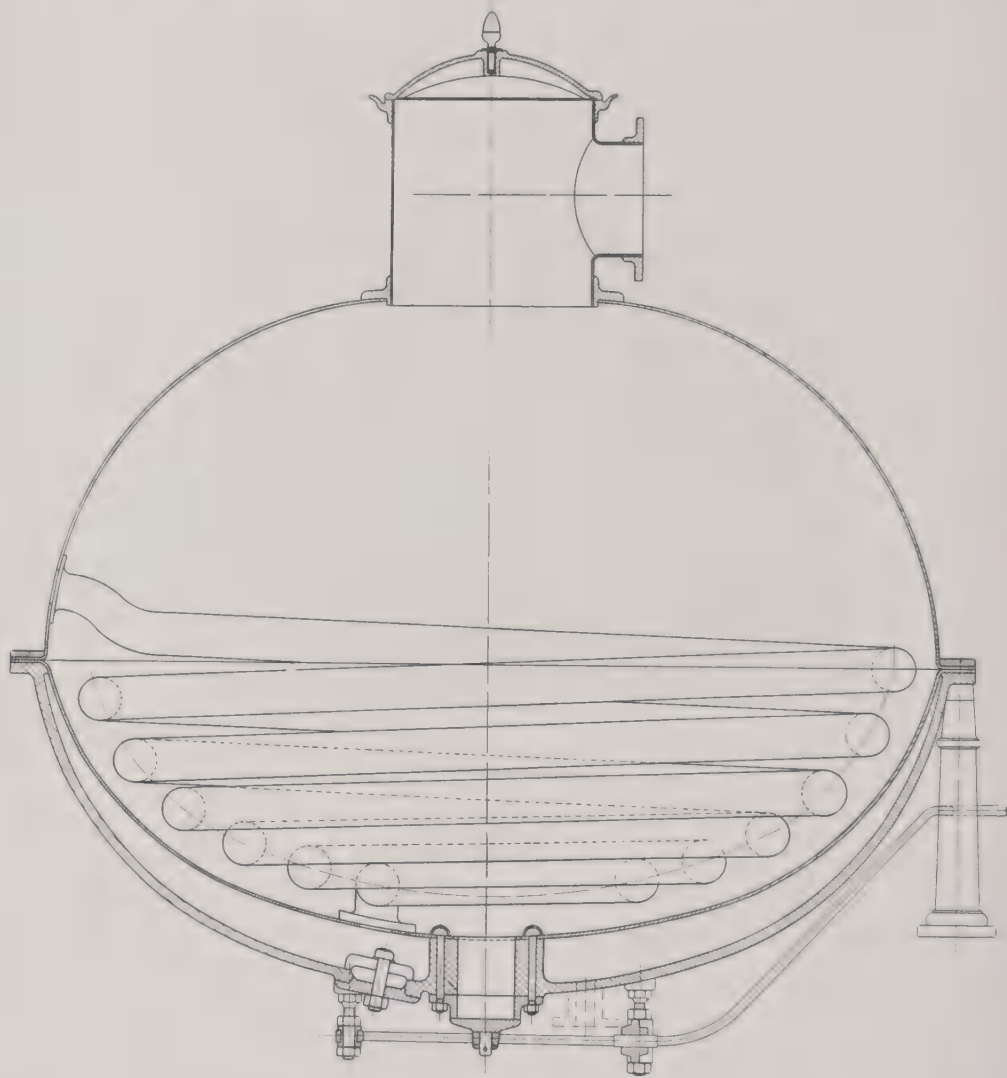
This inefficiency in operation is primarily the result of accepting an insufficient desugaring of the boiling. The master boiler who is in charge of the crystallization process is usually able by the application of a number of tricks and by adding to his pans syrups, *A*-molasses or *B*-molasses, as it may be, to arrive at a certain *n* purity for the finished boiling but which is lacking the consequent and rational application of the fundamental principles of crystallization.

The 4-boiling system can become a necessity in cane sugar factories where the final sugar is remelted after affination, or by the application of the carbonation process when the first boilings have a purity substantially above 90. If such factories are not equipped in the crystallizer station with appropriate cooling systems, it is evident that when the crystal yield % pol in boiling is not more than 50%, the 4-boiling system must be adopted to arrive at a purity for the final boilings of approximately 60.

5. Development of the Technology of Sugar Crystallization

The development in sugar crystallization has four important aspects.

(1) The equipment to be used in the crystallization process: pans, vacuum system.¹ In Fig. 9/3 we give a picture of one of the first vacuum pans as



Courtesy Stork-Werkspaar

Fig. 9/3a. Cross-sectional view of VAN VLISSINGEN pan. Diameter pan 7'6", diameter coil 3½", thickness of the shell constructed in copper 5/16", massecuite discharge valve 57/8", thickness of the double bottom constructed in cast iron 23 mm.

introduced in many countries for the crystallization of granulated sugar under vacuum. This is the so called VAN VLISSINGEN pan. In Fig. 9/3a we give a cross-sectional drawing of the original VAN VLISSINGEN pan. In Fig. 9/4 we give a picture of a modern vacuum pan as made by GEORGE

FLETCHER & CO. LTD., Derby, England, and in Fig. 9/4a a crosssectional view of this type of pan showing the design of calandria, center well, discharge valve, catch all and the overall dimensions.

(2) The operational technique for the crystallization process including standardization of the raw materials to be crystallized as to temperature

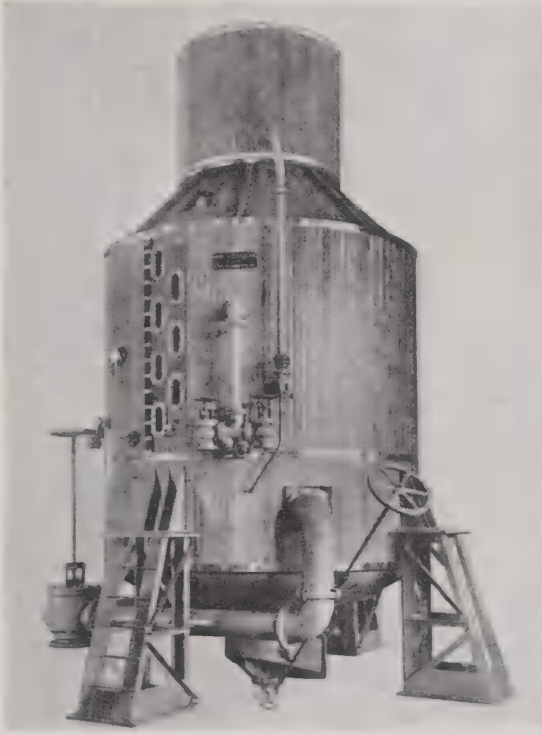


Fig. 9/4. FLETCHER vacuum pan.

and concentration, standardization of steam and vapor pressures to be used for heating and evaporation, standardization and adjustment of vacuum.

(3) Control methods to direct and guide the concentration of the solutions to be crystallized as to saturation and supersaturation.

(4) Automatization of the crystallization process.

The progress in the crystallization process over the whole world has been characterized primarily by the introduction of more suitable types of equipment and secondly by the introduction of useful control instruments. The second part of the development is in many countries far behind the development of the equipment. This is to a certain extent the result of a tradition in the operation of sugar mills. The personnel in charge of the pan floor consists primarily of men having a great practical experience in sugar crystallization who consider their skill as a kind of art and their

personal experience the greatest asset for a well conducted crystallization process.

The modern instrumentation which also makes possible an automation of the boiling process, is a denial of the irreplaceable value of personal experience and skill. Our present knowledge of the crystallization process

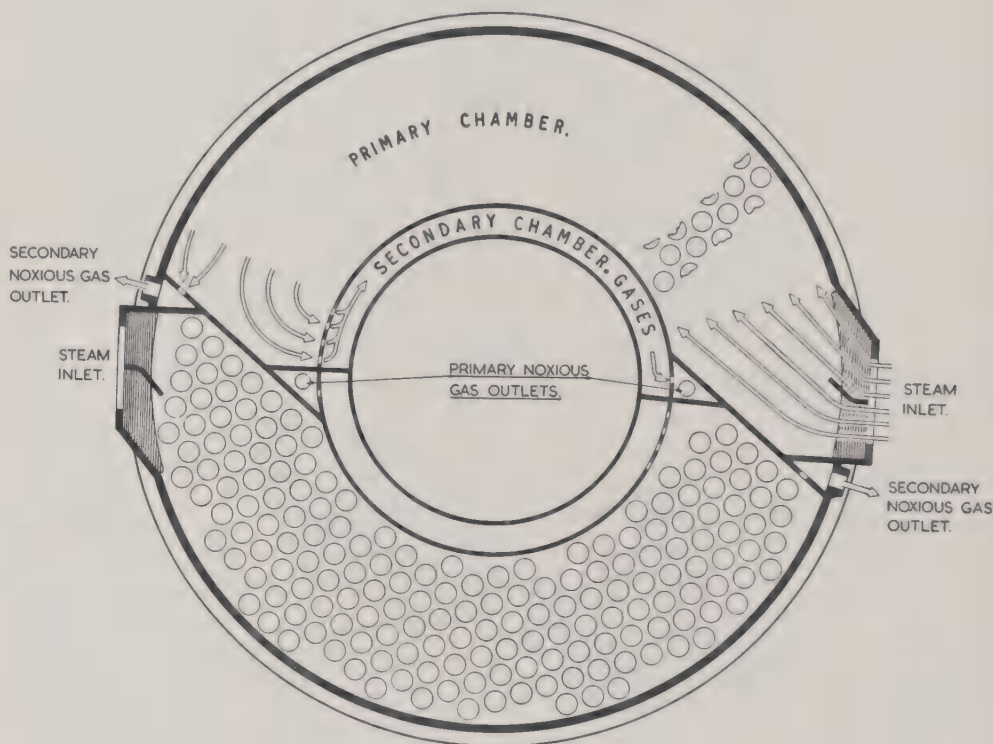


Fig. 9/4a. Cross-sectional view of FLETCHER vacuum pan.

has advanced to such an extent that it can be conducted completely along rational lines eliminating the necessity of personal judgment and subjective manipulations. This creates a conflict found in all industries where the mastership of the experienced craftsmen is replaced by scientifically controlled operational conditions.

The variables in the crystallization process are: temperature, vacuum, rate of evaporation, purity of raw materials and mother liquor, supersaturation. The progress is to reduce the number of variables in a technological operation to a minimum and to standardize them at uniform values which according to the experience have demonstrated constant results.

In a summarized form the development of the sugar crystallization is as follows:

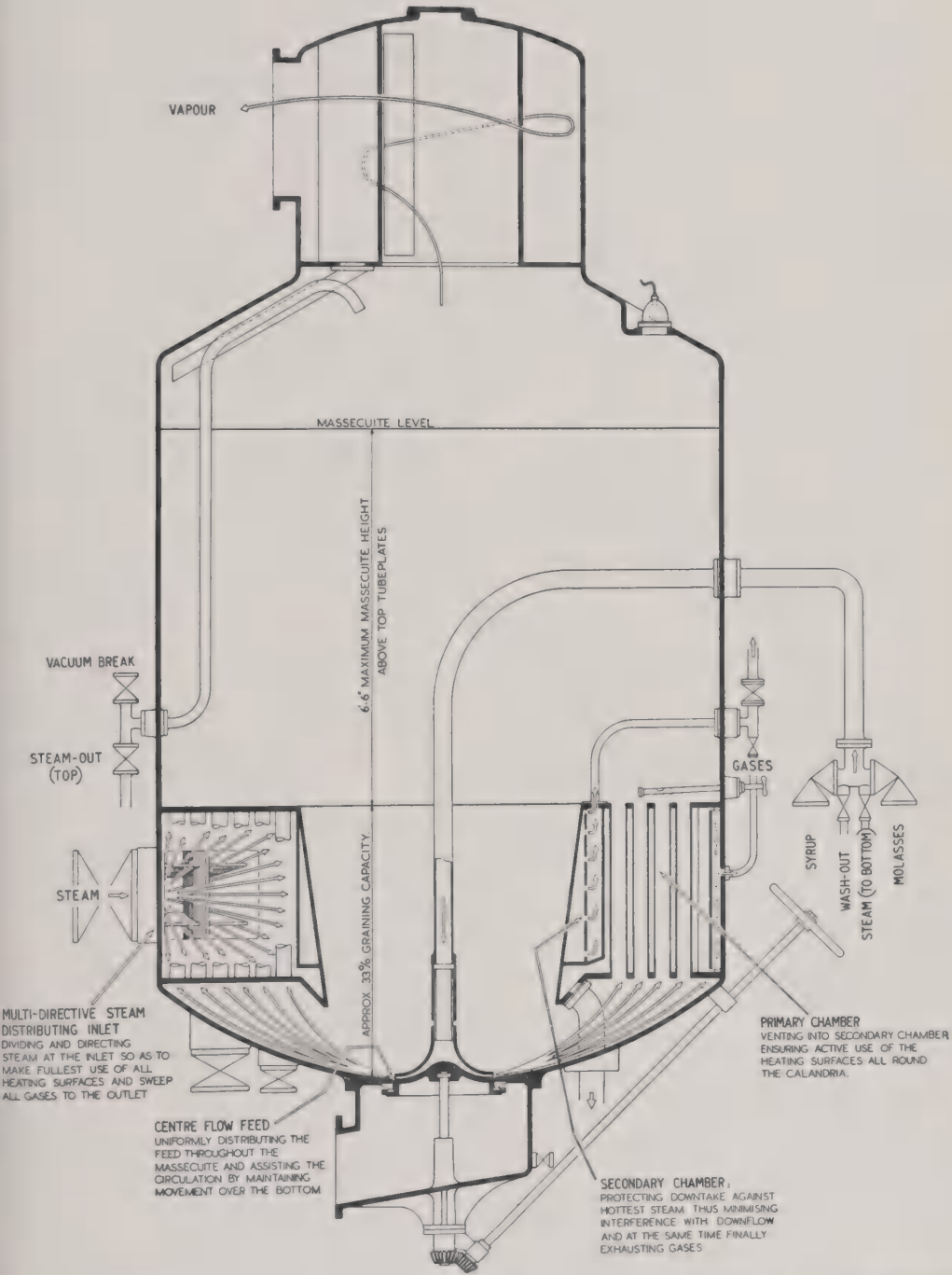


Fig. 9/4b. Cross-section of a modern calandria pan as designed and constructed by George Fletcher & Co., Ltd., Derby, England.

CONSTRUCTION DETAILS OF CRYSTALLIZATION (PAN) EQUIPMENT

Volume dimensions of pans

	minimum	maximum
Net volume of strike	450 cub. ft. (130 hl)	2400 cub. ft. (680 hl)
Diameter of pan	7'	20'
Maximum height of massecuite level above calandria	5'	8'
Vapor outlet	18"	42"
Center downtake diameter	$\frac{1}{4}$ of pan diam.	40% of pan diam.

Construction material

Shell	Steel plate or cast iron.
Calandria $\left\{ \begin{array}{l} \text{tubes} \\ \text{tube sheets} \end{array} \right.$	Copper or brass. Steel, stainless steel or copper clad steel, bronze or copper.
Piping and pipe connections	Steel, cast iron or copper.

Bottom construction

	minimum	maximum
Conical design of bottom, angle	20°	35°
Minimum distance bottom at periphery to lower tube sheet of calandria	8"	1' 4"
Sufficient working space for inspection and repair of tubing of calandria, or bottom of pan must be able to lower for maintenance work.		
Sufficiently dimensioned manhole in bottom or a manhole has to be made in shell above calandria.		
Discharge valve diameter	14"	2'
Special point to be considered	Bottom discharge valve to be constructed as double valve.	

Heating surface (calandria type)

	minimum	maximum
Heating surface per unit volume of massecuite	1 sq. ft./cub. ft. (0.33 m ² /hl)	2 sq. ft./cub. ft. (0.65 m ² /hl)
Height of tubes	3'	5'
Diameter of tubes	3"	4.5"
Steam or vapor inlet	8"	16"
Condensate removal	Single drain going downward through bottom or exterior condensate drain.	
Removal of non-condensable gases (venting)	Gas vents have to be connected with vacuum.	

Cleaning of pans

After each strike

Special arrangements

Periodic cleaning of pan

Vacuum

Vapor or steam

Feeding arrangement

Instrumentation

1. By spray nozzle using hot water or a mixture of water and steam.
2. Steamings and washings of pans have to be separated from discharged masse-cuite crystallizer.

It must be possible to boil the pan out with water at least once a week. Water inlet and outlet must be well dimensioned for quick filling and discharging of pan. This operation is essential for maintaining perfectly clean evaporating surfaces.

1. Must be adjustable.
2. Must be maintained at a constant predetermined value.
3. Must be at least 27.9" mercury (70.8 cm) for last product pans (1 lb/sq. inch = 0.07 kg/cm² absolute pressure).
4. Must be recorded.

1. Pressure must be constant.
2. Must be adjustable between predetermined values.
3. Must be recorded.

4. Must be free of oil and mechanical dirt.
1. Feed valves must be standardized.
2. Materials fed to the pan must be free of grain by proper dilution and have a temperature as close as possible to temperature of the pan content (65° C).

3. The feed of the pan must be introduced in such a way that it does not interfere with the pan circulation.
4. The feed outlet in the pan must be under the heating surface (never above the heating surface).
5. All pans should have a water inlet for washing, ripening of seed grain and for finishing the strikes to maintain sufficient evaporation per unit of time for circulation of the pan content (movement water).

1. All pans must be equipped with a thermometer to measure the temperature of the pan content, preferably recording; the temperature must be measured at least 8" from the pan wall and 8" above the upper tube sheet.

2. All pans must be equipped with at least one vacuum gauge, a direct reading mercury barometric vacuum meter, the second a recording vacuum meter.
3. All pans must be equipped with an instrument to determine the supersaturation, based on boiling point elevation, refractometer brix of mother liquor (pan refractometer), electrical conductivity (cuitometer), heat transfer meters or power consumption meters of mechanical circulators.
4. A proof stick for sampling pan content.
5. A magnifier to observe the developments and characteristics of the formed grain.

The results of the crystallization process in well designed sugar factories are a reduction in the time required for producing sugar in a crystalline state of a predetermined crystal size and an increased yield of recovered crystallized sugar per 100 sugar in material to be subjected to crystallization. The consequences of these both factors are that the performance per unit of equipment can be increased, the uniformity of the resulting product improved, and the operational control simplified.

As an indication of what can be obtained in modern sugar factories we must set the following standards which are based on actual factory experience where the conditions according to our present knowledge should be considered the best.

PROGRESS IN SUGAR BOILING

Obtainable results with modern equipment, good control instruments and efficient operation

Fine granulated in refineries	Time of boiling sugar strikes
Raw sugar boilings, purity 80-90, starting with feeding of <i>C</i> -sugar magma	one hour
Raw sugar boilings, purity 65-80, starting with footing of <i>C</i> -sugar magma	two hours
<i>C</i> -sugar boiling in cane sugar factories, purity 58-65, starting with footing of grained <i>A</i> -molasses	three hours
	four hours

	Recovered crystal yield % pol in massecuite	Recovered crystal yield % massecuite
Refined sugar strikes	65	60
Commercial boilings		
in raw sugar factories, purity 80-90	65	50
in raw sugar factories, purity 65-80	70	45
C-sugar strikes	75	40

6. The Crystallization Installation Consists of a Number of Interrelated Equipment Units

To obtain a maximum yield of sugar in crystalline form, the crystallization process in a vacuum pan can be combined successfully with a cooling of the massecuites in specially designed crystallizers. The idea of improving the crystallization efficiency by subjecting the massecuites to a cooling process in crystallizers equipped with heat exchange elements is an old idea in the sugar industry which has been practiced in many countries and as a rule with satisfactory results. Well known types of special crystallizers are: RAGOT & TOURNEUR, KARLIK-CZAPIKOWSKY, SCHNEIDER, LAFEUILLE, WERKSPoor (Figs. 9/5 and 9/6).^{2,3}

LAFEUILLE has introduced in the sugar industry an apparatus that could be used as the vacuum pan for normal boiling and where the heating surface

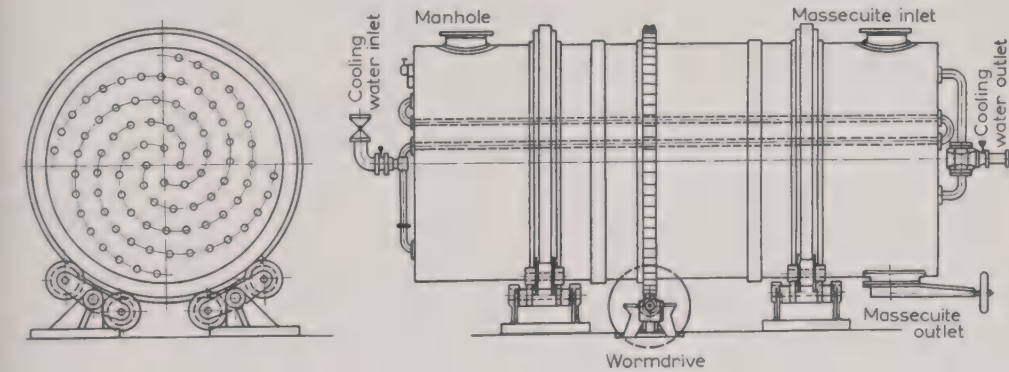


Fig. 9/5. LAFEUILLE rotary crystallizer.
Fig. 9/6. Cross-section of LAFEUILLE rotary crystallizer.

could be used after the strike had been concentrated to the final density as well as heat exchange element to cool the massecuite to increase the crystal recovery. This equipment is called the LAFEUILLE cuiseur. It has found only a limited application in the sugar industry. The total number of cuiseurs installed around 1928-1930 was 13.

The effect of a high yield of crystallized sugar is in the first place a simplification of the boiling process. In the second place, a reduction in the amount of massecuite that must be handled by the centrifugal station. As an example, we have calculated, in Tables 1 and 2 for a capacity of 100 metric tons of cane per 24 hours and a syrup purity of 84.3, the amount of massecuite produced using crystallizers for the commercial boilings acting as storage reservoirs and a 4-boiling scheme. In comparison the handling

TABLE 1
4-BOILING SYSTEM (ORDINARY CRYSTALLIZERS)

	hl	Brix	Purity	Purity molasses	Purity mc.-purity molasses	Crystal yield % pol in mc.
Syrup	2000	60.0	84.3	—	—	—
1st massecuite	808	92.0	84.3	65.7	18.6	54.2
2nd massecuite	553	94.0	72.8	53.5	19.3	41.5
3rd massecuite	488	96.0	64.9	45.4	19.5	35.7
Final massecuite	428	98.2	57.1	29.3	27.8	38.5
C-sugar magma	—	87.5	84.3	—	—	—
Commercial sugar	—	—	98.7	—	—	—
C-sugar	—	—	84.3	—	—	—
hl undiluted molasses from centrifugals	1060	—	—	—	—	—

TABLE 2
3-BOILING SYSTEM (RAPID COOLING CRYSTALLIZERS FOR A AND B BOILINGS)

	hl	Brix	Purity	Purity molasses	Purity mc.-purity molasses	Crystal yield % pol in mc.
Syrup	2000	60.0	84.3	—	—	—
1st massecuite	982	92.0	84.3	60.7	23.6	60.1
2nd massecuite	572	96.0	69.9	45.4	24.5	44.9
Final massecuite	427	98.2	57.1	29.3	27.8	38.5
C-sugar magma	—	87.5	84.3	—	—	—
Commercial sugar	—	—	98.7	—	—	—
C-sugar	—	—	84.3	—	—	—
hl undiluted molasses from centrifugals	765	—	—	—	—	—

of the commercial boilings in crystallizers with cooling elements in which the *A*- and *B*-boilings were cooled to a temperature of 55° C and a desugara-tion from syrup to final molasses in 3 boilings. The data given in these tables are averages from a number of factory reports collected in Java between 1928 and 1937. The figures represent crop averages of at least

ten mills for each of the two systems: (a) 4-boiling scheme with ordinary crystals, (b) 3-boiling scheme with the application of crystallizers with heat exchange elements for first and second boiling.

In Fig. 9/7 is represented the effect of cooling of massecuite on crystal % pol in massecuite for a massecuite of 77 purity which had been kept for

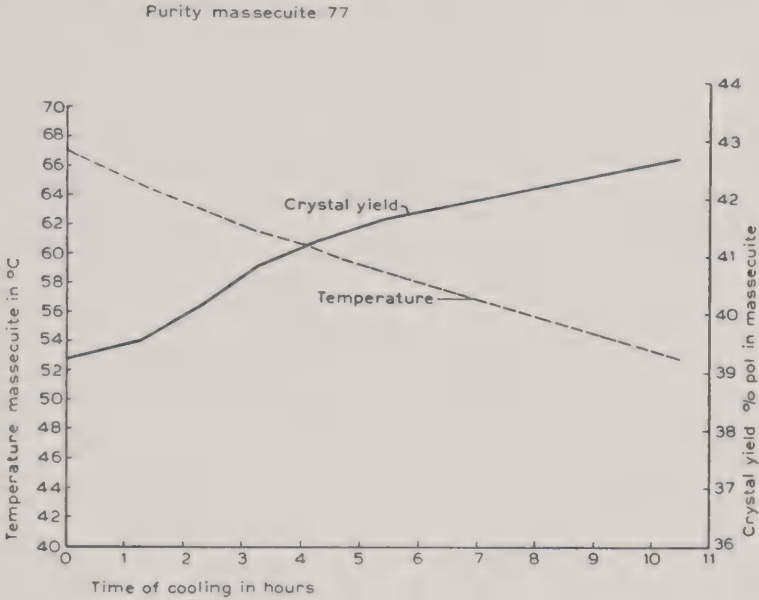


Fig. 9/7. Effect of cooling of massecuite in standard U-shaped crystallizer on crystal yield.

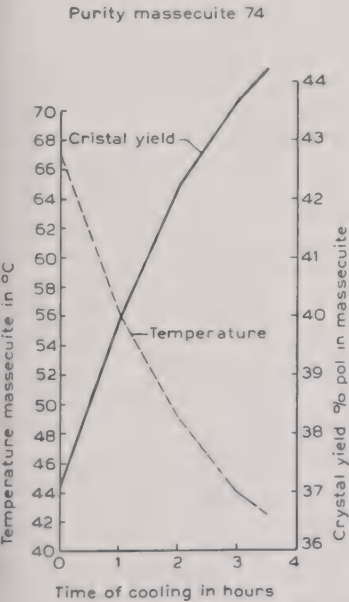


Fig. 9/8. Effect of cooling of massecuite in rapid cooling WERKSPOR crystallizer on crystal yield.

11 hours in a normal U-shaped crystallizer. As a comparison, in Fig. 9/8 the relation is given between the temperature of the massecuite and crystal content % pol for a massecuite of 74 purity treated in a rapid cooling crystallizer. The cooling effect in a crystallizer with heat exchange element is in 3½ hours considerably greater than cooling in an ordinary crystallizer during 11 hours. At this purity of the massecuite it can be observed that the increase in crystal yield % pol follows closely the decrease of temperature of the massecuite.

It is a general experience that the massecuites producing the commercial sugar with a purity range of 75–90 can be cooled in a rapid cooling crystallizer with an appreciable increase in crystal content without the danger of the formation of secondary grain or a too high supersaturation of

the resulting molasses. The cooling of the final boilings delivering the final molasses requires a special technology for massecuites of 58–62 purity in cane sugar factories. It is necessary that the rate of cooling is adjusted to the rate of crystallization. If the cooling is done too rapidly there is the danger of a too high supersaturation with a correspondingly increased viscosity and a reduction in the rate of crystallization. This subject will be discussed in the Chapters 12 and 13 of this Volume.

7. Fundamentals in the Practice of Sugar Boiling

The modern sugar industry has tremendous variations in design and size of vacuum pans. The smallest type of vacuum pan installed in modern factories, usually built towards the end of the last century or the beginning of this century, is a pan with a net volume of 50 hl constructed of copper. It is used today in some factories for graining or making the footing for commercial boiling but no more for making finished sugar strikes. Discussions among technologists as to the preference for coil pans or calandria pans have to a certain extent been solved in recent years in favor of the calandria pan, which has as advantage a larger capacity per 24 hours and the possibility to boil the strikes on exhaust steam of low pressure or on vapors taken from the evaporators. Another advantage is the simplicity of construction.

All the discussions on the different types of pan bring up the point of the circulation in pans.⁴ The ideal of a vacuum pan is that all the conditions of the massecuite in process of crystallization be as uniform as possible as to density, crystal content, supersaturation and temperature, and to have these conditions uniform through the whole pan content. This ideal is never fully realized. We must accept certain differences resulting from the heating and evaporation but these deviations of the average as to temperature and supersaturation must be kept within certain limits. The ideal of a pan that it can be classified as a pan with a good circulation is that the temperature differences as they are measured as the temperature differences of the massecuite under the calandria and measured 40 cm above the calandria, when the pan has reached practically its final volume of massecuite, should be no more than 3° C (5.5° F).

The circulation in pans is a result of the difference in specific gravity of the massecuite evaporating in the top layer above the heating surfaces and the specific gravity of the massecuite in the returning downflow of the massecuite through the center well or downtake. This is indicated schematically in Fig. 9/9.

It is possible to calculate, via the amount of heat transferred per unit of time from the heating medium (steam or vapor) to the massecuite and the measured temperature differences in the massecuite, the flow of the massecuite through the tubes of the calandria or between the coils of a coil pan and to get an impression of the rate of circulation of a massecuite during

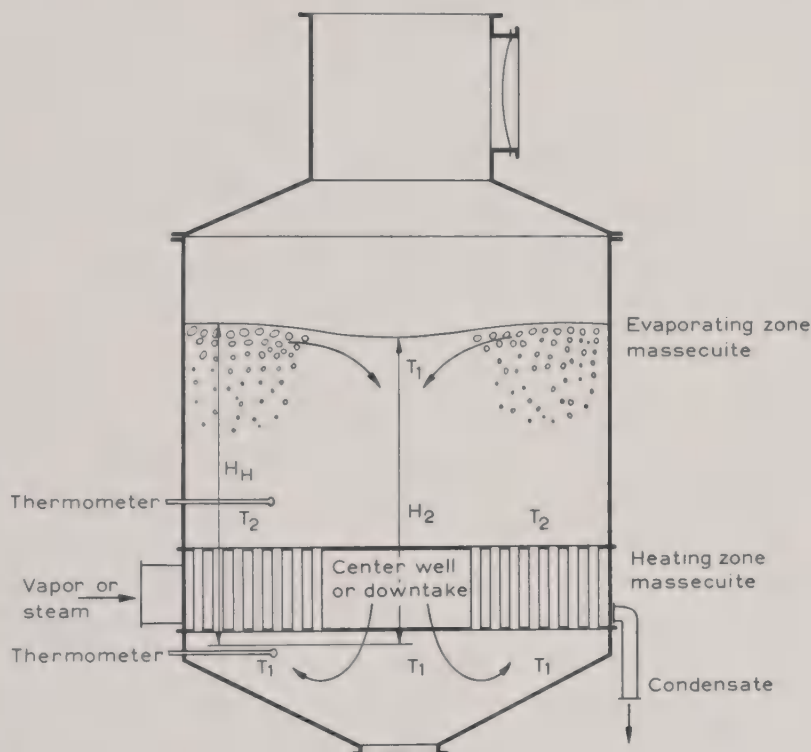


Fig. 9/9. Schematic drawing of the mechanism of heating, evaporation and circulation in a vacuum pan. The intensity of circulation or the flow of massecuite through the tubes of the calandria is determined via the temperature difference $T_2 - T_1$. The quantitative relationship is: $(T_2 - T_1) \times \text{specific heat per liter of massecuite} \times \text{volume of massecuite in liters flowing per minute through the calandria tubes} = \text{condensate in liters per minute} \times \text{condensation heat of vapor per kg}$.

It is also possible to express the intensity of circulation at the rate of flow of massecuite in dm or m per minute flowing through the calandria tubes, to be calculated by the equation: $\text{volume of massecuite in liters per minute} = \text{rate of flow of massecuite in dm per minute} \times \text{cross-sectional area of calandria tubes in dm}^2$.

the crystallization process which can be expressed in feet per second or meters per minute.

Definition of Circulation

In the technical literature on the boiling process, frequently the expression is used: 'circulation in vacuum pans'. This expression is usually applied to describe in a qualitative way the intensity with which the massecuite is

moving upwards along the heating surfaces and evaporating in the upper level zone and returning downward to the bottom of the pan via the center well or downtake. The driving force for the circulation is the intensity of evaporation or the formation of vapor bubbles in the upper zone level causing a lower specific gravity of the fillmass and creating different hydrostatic pressures above the heating surface and the massecuite level above the downtake. The driving force $[F]$ can be expressed in a mathematical way as follows:

$F = \text{height of massecuite measured from lower tube sheet of calandria} \times \text{average specific gravity of massecuite plus vapor bubbles as present in an operating pan above the heating surface of the calandria} \times \text{cross-sectional area of the calandria} - \text{height of massecuite measured from lowest center of downtake} \times \text{specific gravity of massecuite} \times \text{cross-sectional area of downtake}.$

An unknown factor in this equation is the specific gravity of a boiling massecuite, respectively the mixture of massecuite and vapor bubbles.

We have tried to get an impression of the volume of vapor bubbles in the boiling massecuite in vacuum pans, when they are operating under normal factory conditions, by closing the vapor inlet valve to the calandria and to estimate the reduction in volume of a massecuite when the boiling process is interrupted. This reduction in volume represents the volume of vapor bubbles in massecuite present in the evaporating massecuite in the upper zone level and makes it possible to calculate the average specific gravity of the massecuite when a pan is in operation.

According to these experiments the driving force pushing the massecuite through the tubes of the calandria is, for well designed vacuum pans for *A*- and *B*-boilings, measured at the inlet at the lower tube sheet of the calandria, 2 to 3 kg per dm². The rate or intensity of circulation can be expressed as the flow speed of the massecuite passing through the calandria tubes. For commercial raw sugar boilings the flow speed is 5 to 20 m per minute in well designed pans during the building up of a strike.

For a better understanding of the circulation phenomena we can use the simple expression

$$\text{rate of circulation} = \frac{\text{driving force}}{\text{resistance}}$$

The resistance in pan circulation depends on pan design (flow resistance surfaces) and viscosity of massecuite.

It is possible in this way to calculate the circulation of pans in a quantitative way and to analyze the factors determining the intensity of circulation.

Two definitions are used for circulation. The circulation of a pan is

the percentage of the total volume of massecuite circulating per minute through the heating elements of the calandria. In a good circulating pan the whole massecuite volume is passing through the heating elements in 1 minute time. This is called a circulation = 100. If it takes 4 minutes for a pan to circulate the whole pan content through the heating elements, the circulation of the pan is 25. The second definition that is used to describe quantitative circulation is the flow rate in meters per minute of the massecuite flowing upwards through the calandria tubes.

As an example of the rate of circulation determined in calandria pans we give the following data: calandria pan with net massecuite volume 300 hl, evaporating surface 150 m², calandria tubes 4" i.d., number of tubes 280.⁵

The amount of condensate measured during the experiment varied from 60 to 180 kg per minute. The temperature difference of the massecuite before and after passing the calandria tubes (measured 15 cm below the lower tube sheet and 50 cm above the upper tube sheet) was 2.8° C. The amount of heat transferred from vapor to massecuite varied per minute from 36,000 to 108,000 kcal (condensate in kg/min × condensation heat of vapor/kg). The specific heat of the massecuite in process was 45,000 kcal (volume of massecuite in liters × specific gravity × specific heat of massecuite). The circulation per minute was $\frac{36,000 \text{ to } 108,000}{2.8 \times 45,000} = 0.3 - 1$. This means that the total pan content during this experiment circulated under the best conditions with a circulation intensity of 100 and with the lowest evaporation rate 30.

This experiment was done with intermittent feeding of pans and demonstrated the irregularity introduced by this system of feeding.

To calculate the flow rate of the massecuite in the calandria tubes we have the following cross-sectional area of the tubes in the calandria: number of tubes × cross-sectional area per tube, 4" i.d. = 280 × 0,81 dm² = 227 dm².

The flow rate of the massecuite through the calandria tubes =
circulating massecuite volume per minute in liters or in numbers:
cross-sectional area of calandria tubes in dm²
 $\frac{7,500 \text{ to } 25,000}{227} = 33 \text{ to } 110 \text{ dm or } 3.3 \text{ to } 11 \text{ m per minute.}$

Studies of this kind were made between 1927 and 1935 with all types of pan design in Java as they have been made along similar lines in other countries. These studies resulted in certain conclusions as to some of the fundamentals that had to be incorporated in the design of a well functioning factory pan. This refers to the dimension of tubes in the calandria, the di-

mentioning of the center well, the design of the bottom of the pan and the intake of the raw materials to be crystallized.

At the present moment the high narrow vacuum pan is a relict of the past. The narrow center well has only a historical interest. The long tubes in a calandria are more a disadvantage than an advantage. The criteria as given in the preceding paragraph must be taken as absolutely essential for modern pan design.

Scientific studies on crystallization have taught us that progress in crystallization can only be made if we are able to control the operational conditions.⁶ The vacuum is one of the most important operational conditions. This must be maintained at a constant value. All modern designs of a pan station should indicate them constructed preferably with an individual condenser and an individual vacuum system so that the charging or discharging of one pan is not influencing the operation in the other pans. The pressure of steam or vapor must be constant. This is in many cases not simple. A technical solution for the fluctuating steam consumption of the pan station is the installation of steam accumulators thereby making it possible that the steam generator plant is operating under uniform and constant conditions. The accumulator acts as compensation for the irregularities in the steam consumption.

Modern control instruments are becoming an absolute necessity when we wish to arrive at the best technical performance. Vacuum meters, thermometers, conductivity control instruments and eventually instruments for measuring the boiling point elevation must be considered a normal and essential part of the crystallization station.

It must be understood that trying to achieve perfection in the technology of crystallization requires that all elements of this technological process be given due consideration. It is, of course, an impossibility to talk about modern instrumentation and to expect miracles from such control instruments if the vacuum of a pan or the steam pressure used for boiling is fluctuating all the time.

There is no secret in the progress of modern technology, but there is a fundamental rule that never should be forgotten and which must consequently be applied. This rule is that we must work on uniformly controllable operational conditions. If a workman in charge of the pan operation must make first class boilings but the steam pressure fluctuates between 3 and 15 lbs. or the vacuum fluctuates between 23" and 25", it is asking for the impossible to expect under such conditions that a massecuite will be produced of absolutely uniform crystals and with a high yield of commercial sugar.

8. The Significance of Circulation on Supersaturation

In the crystallization process in vacuum pans a proper circulation is essential for maintaining uniform conditions as to supersaturation and obtaining a high crystallization rate per unit of time. In Table 3 we have calculated, as an example, the effect of a stagnate massecuite in a vacuum pan, heated via a calandria which as a result of a drop in the vacuum at a certain moment was interrupted in normal evaporation and the resulting circulation. This calculation is done for a refinery strike, brix 88, supersaturation 1.20, vacuum 66.7 cm mercury.

TABLE 3

BOILING POINT TEMPERATURES OF MASSECUITE AT DIFFERENT DEPTHS OF THE BOILING MASSECUITE BELOW THE SURFACE LEVEL FOR REFINED SUGAR LIQUOR, PURITY 100, BRIX 88, SUPERSATURATION 1.20, VACUUM 66.7 cm Hg

Depth below massec. level in cm	Hydrostatic height in cm Hg	Vacuum of the boiling massec. in cm Hg	Boiling point temperature of boiling massec. in °C	State of saturation
0	0	66.7	58.6	1.20
25	2.7	64.0	63.5	1.14
50	5.4	61.3	68.0	1.08
75	8.1	58.6	71.5	1.04
100	10.8	55.9	74.5	saturated
125	13.5	53.2	77.5	0.97
150	16.2	50.5	80.0	0.94
175	18.9	47.8	82.0	0.91
200	21.6	45.1	84.0	0.89
225	24.3	42.4	86.0	0.87
250	27.0	39.7	88.0	0.84
275	29.7	37.0	89.9	0.81
300	32.4	34.3	91.7	0.78

This calculation is, of course, excessive because it is calculated under the assumption that there is no circulation at all. In practice we have found with calandria pans that the temperature difference was 6° C measured 15 cm above the upper tube sheet and 140 cm above the upper tube sheet, with a distance of only 125 cm. This temperature difference corresponds with a difference in supersaturation of at least 0.10.

Careful observation of the crystal structure in pans with poor circulation shows that without any doubt during a part of the circulation of the pans some of the crystals have been exposed to undersaturated conditions and are partly dissolved, which has been corrected in another phase of the crystallization process.

The effect of poor circulation is that it is impossible to discuss the existing conditions during the crystallization process. The supersaturation varies

in a short time from a very high value in the upper level of the massecuite above the heating surface to an extremely low level after the massecuite has left the tubes of the calandria. These great differences occur particularly in the last phase of the boiling process, but this last phase is extremely important for the quality and yield of sugar to be recovered in the centrifugals.

9. Feeding of Pans

The vacuum pan is connected with syrup in molasses tanks, respectively liquor tanks, and is introduced in the pan via the pressure differences of these tanks and the vacuum in the pan.

The intake in a pan is not only the feeding with the materials to be crystallized, but in raw sugar factories also the magma, being a mixture of fine grain last product sugars and syrup, powdered sugar, or a fine granulated sugar which must grow in the commercial boilings to crystals of a desired size.

The experience is that the intake of sugar in dry form as powdered sugar for seeding a pan or as fine granulated for making coarse crystals is always connected with a certain risk, as the air flow coming into the pan with a powdered sugar passes through the syrup or molasses in the pan and carries a large part of the dry sugar with it, disappearing in the vacuum system. When a pan must be grained with powdered sugar it is recommendable to add this powdered sugar dispersed in a liquid either saturated sugar solution, denatured alcohol, gasoline, or isopropyl alcohol. In this way it is possible to introduce the sugar quantitatively into the footing in the pan.

Another important point in the crystallization process is that the pan must always be connected with an intake for water. This can be necessary for reducing the supersaturation and dissolving secondary grain if this has been formed, or it is sometimes necessary to maintain a certain circulation because the circulation is directly proportional to the amount of water evaporated per unit of time. The driving force for circulation in pans are the evaporation and the vapor bubbles formed in the top layer of the massecuite creating a difference in weight between the massecuite column in and above the heating surface, in the center well or downtake of the pan.

The ideal for feeding a pan is the continuous intake because this creates uniform and controllable conditions for the crystallization process.

The common practice in judging the supersaturation is in most factories still by visual observation of a sample of the massecuite or footing taken

with a proof stick and determining by the index and thumb proof, the string proof, the viscosity. This control system of touch has given the experienced sugar boiler astonishing confidence in judging the degree of supersaturation. The introduction of the electrical conductivity which is based on the very simple relation that the viscosity is proportional to the reciprocal value of the electrical conductivity, has given us a much more accurate and objective system of control than the index and thumb proof of the sugar boiler.

We have had the opportunity to test approximately 50 experienced sugar boilers in Java. We asked them to indicate for us the saturation point of different raw materials, the danger point as to supersaturation that secondary grain could be formed, and to tell us when a raw material was still in a state of undersaturation. These boilers had experience in sugar boiling of many years. We have been using control instruments to check the judgment of these experienced men. The result of this investigation was that not even 20% of the boilers was able to estimate the saturation point of boilings. They could be inaccurate as much as 0.25 in supersaturation. The danger zone for the formation of secondary grain varied for first boilings in a purity range of 80–85 to 1.10 to 1.90 supersaturation. No regularity at all was discovered in the subjective opinions of these experienced men.

The introduction of the electrical conductivity control with proper education on the use of the pan boiler and after overcoming the natural reluctance of skilled craftsmen to adopt a control system, which requires a tremendous amount of patience and demonstration that with control instruments an average sugar chemist can be taught in three days time to make a perfect boiling, made it possible to introduce this control system as a universally adopted system in the Java sugar industry between 1932 and 1940.

The introduction of this control system has not only to overcome the traditional reluctance of the experienced master boilers who feel that it is an infringement of more or less their sacred field of authority, but also to convince the technologists who by their training should have an understanding how progress must be made that such a control method is a step forward. They must be convinced along quite different lines because they wish to know the relationship between supersaturation and electrical conductivity. Undoubtedly, the introduction of a new control method is a stimulant for technological research that we get a better understanding of the conditions of technical crystallization.

The introduction of water movement in pans to maintain a certain level of evaporation during the whole crystallization process because evaporation is the driving force for circulation, requires the convincing of chief engi-

neers that the man on the pan floor is not wasting the steam he has produced. The opinion of many engineers is that all the steam used in pans, especially when they are using extra water, is a waste of valuable fuel. The engineers who have locked off the water valves and the overflow valves from the high pressure steam line to the low pressure steam line are not so exceptional in the sugar industry as it would seem to an outsider.

10. Crystallization of Final Product Boilings

Of the greatest importance for the yield of recovered sugar per 100 raw material as well as for the quality of the commercial sugar when a *C*-sugar is used as seed for the commercial boilings, is the crystallization of the last boiling in plantation white sugar factories, raw sugar factories, and for the recovery also in refineries.

In cane sugar factories the molasses resulting from the preceding boiling has usually a purity between 48 and 60. The concentration of nonsugars in this molasses is extremely high, affecting the rate of crystallization. The supersaturation must be maintained at a rather high level to have a sufficient rate of crystallization per unit of time with a corresponding increase in brix and viscosity of the mother liquor. This results in an operation with a much more viscous material in the pans, reducing the circulation and asking more attention of the operating personnel because by the slower crystallization rate a longer time is required to transfer the sucrose molecules from a dissolved state into a crystalline state.

It is impossible to realize a satisfactory final desugaring of the last product boilings in the vacuum pans directly. This has to be followed by an aftercrystallization in crystallizers, usually today in modern factories with the application of a controlled cooling process by the use of heat exchange elements in these crystallizers.

To obtain a uniform and regular crystal it is customary in most modern mills that the nucleation for the final product boilings is done by seeding a mixture of syrup and molasses with a purity between 65 and 80 by the introduction of powdered sugar or fondant sugar dispersed in an organic liquid (alcohol, isopropyl alcohol, or gasoline).

The manufacture of this seed to be used as nuclei for the crystallization process is a technique in itself. Our personal experience has shown that the best results are obtained by manufacturing a very fine seed slurry by wet milling in ball mills of a refined sugar suspended in an organic solvent having no solubility for sucrose.

The Java sugar industry has been using gasoline as organic fluid because

this is generally available at sugar mills; it is cheap and evaporates completely in the vacuum pans.

The technique of making the final massecuites is that the footing is made in most factories today in a syrup-molasses mixture of a purity between 72 and 78. A low purity of the footing requires considerable time for the growth of the introduced nuclei to a sufficient grain size and obtaining what is called filled or closed footing before the boiling process can switch over to the second phase, being the feeding of the pan with molasses of low purity to build up the strike.

The technique is that the pan is fed with a mixture of syrup and molasses of a predetermined purity and to take care that after concentration the upper tube sheet of the pan is covered to at least 8" with the material to be crystallized to the footing for the final boilings.

The first concentration in modern pans requires 15 to 30 minutes. To judge the supersaturation it is necessary that this either is determined by the boiler by a finger proof, judging the viscosity as an indication of the supersaturation, or by using the conductivity control. When a factory has installed control instruments for determining the electrical conductivity, the measurement of the conductivity is an absolutely reliable system for uniform operational conditions. The supersaturation can be determined by this method with an accuracy of 0.05, which is absolutely sufficient to determine the graining point.

There are two methods of graining by introducing a seed slurry. One is shock seeding where the pan content has been concentrated to a high supersaturation, 1.60–1.70. The other is full seeding where the supersaturation is maintained at a value of 1.30–1.40. The amount of seed slurry to be used is extremely small. To manufacture 1000 cu.ft. (280 hl) of final C-masseccuite, the amount of sugar that must be used resulting from wet milling in an organic fluid is approximately 40 to 50 g. After the introduction of a seed slurry it is usually observed that the supersaturation is still increasing during 3 to 5 minutes after the nuclei have been brought in the footing. It is necessary at this point to start introducing water in the pan immediately to maintain a high rate of evaporation giving a perfect circulation of the footing. This must be continued for 15 to 20 minutes during which time the nuclei are growing rapidly to a visual crystal size filling up the footing and preventing an increase in supersaturation causing the formation of secondary grain and resulting in an uncontrolled crystallization process.

When a sufficient amount of crystals has been formed in the footing, that according to a visual observation it is more or less filled with crystals

which corresponds with a crystal content on footing of 30–35 %, the boiler switches over to feeding the pan with low purity molasses. This process can be controlled accurately via the conductivity control.

In Fig. 9/10 we give a graphical representation of the different phases of the crystallization process.⁷ The feeding of the pan must be done con-

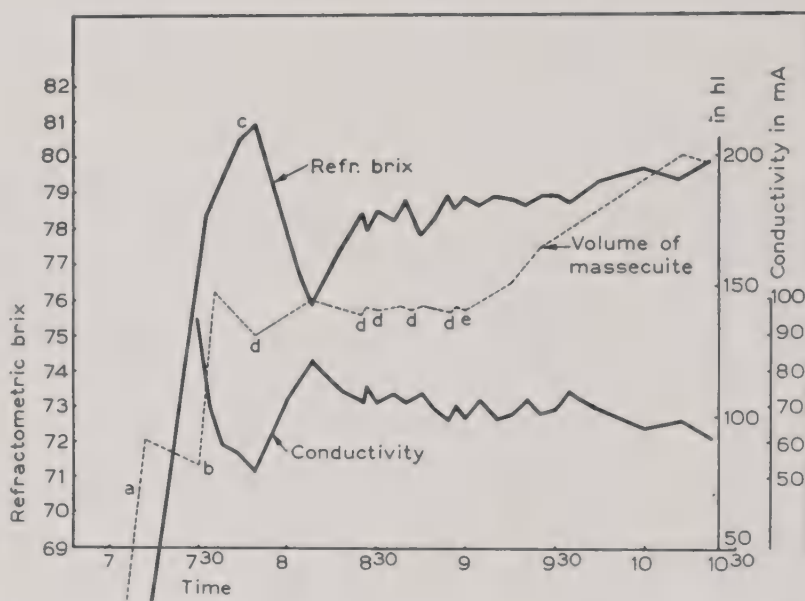


Fig. 9/10. Relation between refractometric brix of mother liquor in boiling massecuite and electrical conductivity of the massecuite.

tinuously. The so-called intermittent feeding of pans is a practice which, in the first place, results in irregular conditions for the crystallization; in the second place according to all the available experience, it increases considerably the total required time for making a massecuite.

With natural circulation the growth of the last product sugars from nuclei to a crystal size of 0.25–0.35 mm linear, which is a common crystal size for the last product sugar, takes approximately 5 to 8 hours in raw sugar factories. It can be reduced in plantation white sugar factories using the carbonation process as the purification method to approximately 4 hours as a result of a different composition of the nonsugars.

In factories where only calandria pans are installed, it is not customary that in one pan the boiling process is executed straight from footing to finished strike to be discharged to the crystallizers. One footing made in a calandria pan is usually sufficient for making three or four finished strikes accomplished by cutting or storing a certain percentage of the unfinished C-strike in a special storage crystallizer. The stored semi-finished strike

is used to start the boiling of another *C*-strike in another pan as soon as it is available.

Extremely important in the *C*-strike is the finishing of the boiling. A *C*-strike should be concentrated to such a water content of the mother liquor that, without any dilution in the crystallizer, a well exhausted final molasses results. This is done by finishing the strike by maintaining a satisfactory circulation in boiling the pan for the last 40 to 70 minutes by the introduction of movement of water. This circulation in the pans at higher temperatures results in a decrease of the supersaturation as a precaution that no secondary grain will be formed when the *C*-massecuite is charged to the crystallizers. It is not recommendable to start immediately with cooling of *C*-massecuites when they have been charged to the crystallizers. They should be left in the crystallizers for 1 to 2 hours without any cooling water in the heat exchange elements to reduce the supersaturation of the mother liquor.

The conductivity of final massecuites must decrease towards the end of the strike. The empirical experience of the boilers, when the pans have been installed with recording conductivity meters, will find easily the correct values for realizing the ideal conditions of crystallization.

This second phase of the boiling of final strikes is of such a character that it can easily be done automatically by connecting the recorder of a conductivity meter with a Servo motor, opening and closing the feed valve charging the pan with the material to be crystallized.

In Fig. 9/11, we give an example of the recorded conductivity of a final product boiling made in a calandria pan with natural circulation.

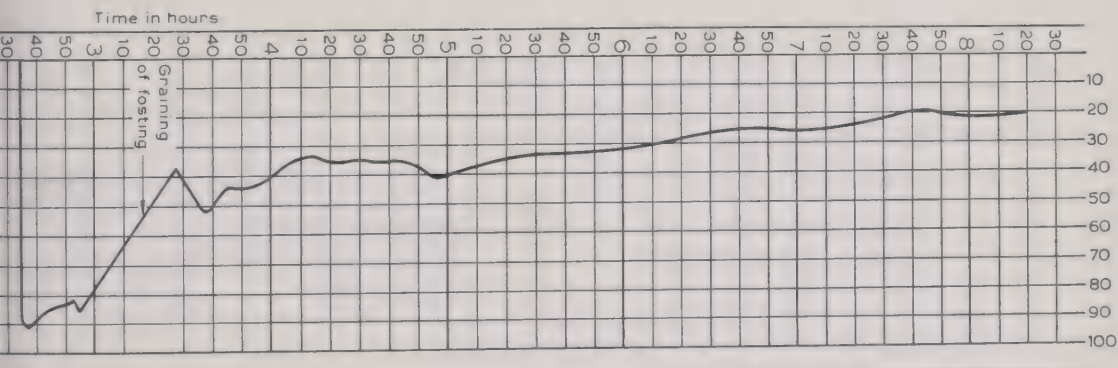


Fig. 9/11. Recorded conductivity in mA of the first part of a *C*-massecuite grained with powdered sugar in a mixture of syrup and *A*-molasses, followed by continuous feeding of the pan with *B*-molasses.

11. Application of Conductivity Control for the Crystallization Process

The application of the determination of the electrical conductivity was introduced in the Java sugar industry for the first time in 1932.⁸ HONIG and NICOLA made a study of the relationship between the electrical conductivity and viscosity of molasses and verified the applicability of the rule of WALDEN, which states that the product of electrical conductivity and viscosity is constant, or in other words, the electrical conductivity is proportional to the reciprocal value of the viscosity.

This investigation was made to study the effect of different purification methods on the viscosity and to see whether the constant in the WALDEN equation could be used as a characteristic value for the viscosity-conductivity ash relation of molasses, respectively could be related to the crystallizing quality of sugar house products of low purity. It was suggested that the same system could be used as an aid in the practical crystallization process. A simple conductivity meter was constructed consisting of a voltage transformer, a set of electrodes and a mA meter. After an investigation at the Java Sugar Experiment Station in 1931, it was introduced for the first time for practical crystallization control in sugar factories in 1932. The system of electrical control was used parallel with a control of the boiling process with a ZEISS pan refractometer. The first results of these experiments are reproduced in Fig. 9/10.

The pan refractometer was an extremely useful instrument for boiling control investigations but it was seen immediately that the use of the conductivity to judge the supersaturation had from a practical point of view great advantages. The advantages are that the instruments required for conductivity control are inexpensive and they are to a certain extent fool-proof. The pan operator can use the direct readings of a mA meter as an indication of the concentration of the pan content.

Already in 1932, ten pans were equipped with conductivity control meters constructed at the Java Sugar Experiment Station. The effect was that the operating personnel was using these instruments after some simple instructions. The reaction of this personnel gave us the confidence that this instrument was a step forward in an objective control system for the crystallization process.

The collective experience showed that the readings of the mA meter, to obtain the best results, varied from factory to factory. This was partly the result of the fact that the capacity of the electrode sets was not standardized. In the second place, the average ash content of the raw materials

varied in Java considerably from factory to factory. Factories near the coast with a higher salt content in the soil have usually a much higher ash content in their juices than the factories in the interior of the island. The critical colleagues among our technologists considered this effect of the nonsugar composition a handicap for an absolute objective control method. A request was made to the Java Sugar Experiment Station to develop a method where a predetermined correction factor could be applied for the ash content of the raw materials and that it would be possible to use the conductivity control only with an adjustment to the purities of the boiling to be made. Furthermore it was requested to give a set of standard supersaturation values related to the specific conductivity of the raw materials which would make it possible that the experience of one factory could be transferred, after the necessary corrections for the ash content, to the conditions existing at other mills.

The history of the electrical conductivity control is that the relationship between viscosity and electrical conductivity, respectively concentration or brix, of a technical sugar solution and conductivity on one hand and viscosity on the other hand was studied systematically for the first time by HONIG and NICOLA in 1928 and 1929. It was found that conductivity could be used for a certain type of material as an indirect figure for the determination of the brix or supersaturation. ALEWIJN developed the first technical control instrument, composed of easily available parts that could be used for the determination of the conductivity in pan operations. ALEWIJN investigated for the first time in 1932 the applicability of this system for practical sugar boiling control.

The technical development of the instruments as a commercial unit has been undertaken in the Netherlands by HEEMAF, Hengelo, and in the United Kingdom under the name of cuitometer by the SUGAR MANUFACTURERS SUPPLY CO. Later on, different types of electrical conductivity control meters have been introduced. As far as we are able to judge the developments of this instrument, they have been based on the first experiments and studies made in the Java sugar industry.

12. The Conductivity of Technical Sugar Solutions at Saturation Point

In 1936 the study on the relationship between the specific conductance of a technical sugar solution and the conductivity of the same solution concentrated to the saturation point at a temperature between 55° and 70° C had progressed to such an extent that it was possible to predetermine

exactly the conductivity of the raw material at the saturation point based on the specific conductance of the same material. It is a well known fact that when a technical sugar solution of high density is diluted, the conductivity increases with the dilution until a maximum conductivity is reached at a brix of approximately 26 to 30. The effect of the degree of dilution on the conductivity of a molasses or syrup is given in Fig. 9/12.

The conductivity of any kind of technical sugar solution at 30° C diluted

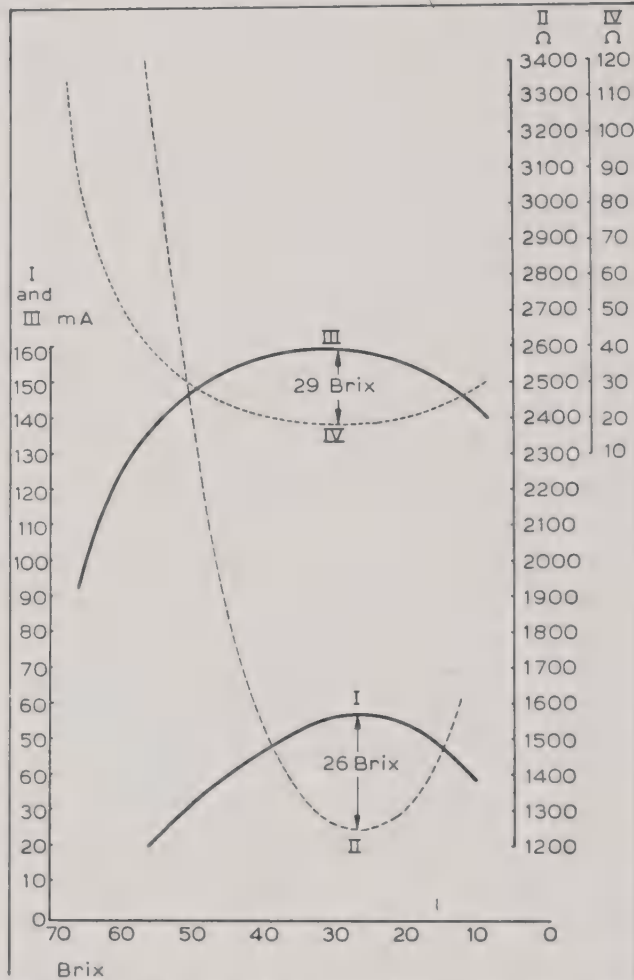


Fig. 9/12. Relation between conductivity, respectively resistance of syrups and molasses at different brix for purities from 40 to 45 (maximum conductivity at 29 brix) and for purities from 85 to 100 (maximum conductivity at 26 brix). The curves I/II have been determined for a purity 99, the curves III/IV for a purity 51. The voltage used for the determination of the conductivity was for I/II 88 V and for II/III 27.5 V.

to 26–29 brix, determined with a brix hydrometer, gives a value for the conductivity called the specific conductance, which is not sensitive for small variations in the brix and which value is directly related to the ash content, respectively to the ash constituents determining the conductivity

of the raw material under the conditions of the crystallization process. The dilutions to be used for the determination of the specific conductance are as follows:

Purity	To be diluted to uncorrected hydrometer brix of
100 — 85	26
85 — 70	27
70 — 55	28
55 — 40	29

} calc. at 30° C

Since the approximate purity of the raw materials on the pan floor is usually well known in all sugar factories, it is simple to dilute volume by volume a certain amount of molasses or syrup as present in the syrup and molasses tanks on the pan floor to obtain the brix required for the determination of the specific conductance. In Table 4 we give the ml of water to be added to 100 ml of the sugar house raw material to be tested for the purity range between 50 and 100 to have the sugar solutions from 26 to 29 brix for the determination of the specific conductance.

TABLE 4
DILUTION TO BE APPLIED WITH SYRUPS AND MOLASSES FOR THE DETERMINATION OF THE SPECIFIC CONDUCTANCE

Brix of syrup or molasses to be tested for specific conductance	To 100 ml of the syrup or molasses to be tested must be added the following amounts of distilled water in ml	dilution to 26 brix	dilution to 27 brix	dilution to 28 brix	dilution to 29 brix
50		113	105	96	89
51		119	110	101	93
52		124	115	106	98
53		129	120	111	103
54		135	125	116	108
55		140	130	121	112
56		145	135	126	117
57		151	141	131	122
58		157	146	136	127
59		162	151	141	132
60		168	157	147	137
61		174	162	152	142
62		179	168	157	147
63		185	173	162	152
64		191	179	168	157
65		197	185	172	163
66		203	190	179	168
67		209	196	184	173
68		215	202	190	179
69		221	208	195	184
70		227	214	201	190

The relationship found was:

$$\frac{\text{specific conductance at } \pm 28 \text{ brix and } 30^{\circ} \text{ C}}{\text{conductivity of the same material at the saturation point between } 55^{\circ} \text{ and } 70^{\circ} \text{ C}} = \frac{6.2}{1}$$

for a purity range of 75–85. For lower purities this ratio decreases slightly, being for 50 purity cane molasses appr. 6.0.

To use this relationship a test electrode was constructed having $\frac{1}{6.2}$ capacity of the electrodes used for the conductivity control in the pans. Fig. 9/13 gives a picture of a test electrode used for the first time in 1936 in Java sugar factories.

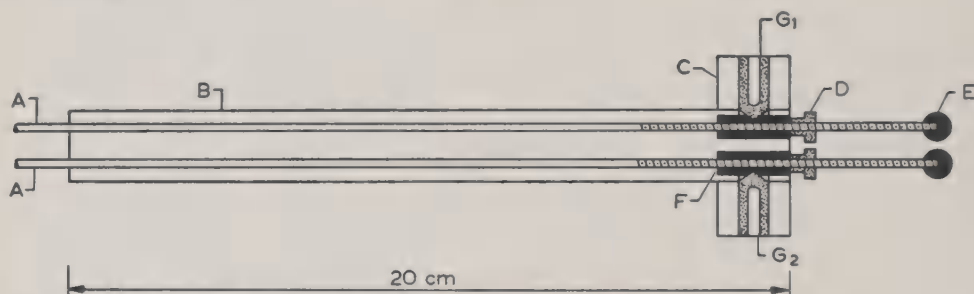


Fig. 9/13. Test electrode as used in the Java sugar industry for the determination of the specific conductance of the materials used in the crystallization process in vacuum pans. The capacity of the electrode set *A A* can be adjusted to the capacity of the electrodes as used in controlling the crystallization process in the vacuum pans.

Construction of the Test Electrode

The test electrode consists of a cylindrical tube with two canals for the electrodes (length appr. 20 cm, diameter 2–3 cm) made from ebonite or other insulating plastic. At one side is a cap into which are inserted the two electrodes adjustable as to length and position via a screw thread that can be calibrated exactly to the desired capacity of the 'conductivity cell'. These two electrodes are connected with normal electric wire and used with the same system of measuring the conductivity for the pan control. When the pan control system is equipped with a voltage regulator, the material to be boiled is first tested on its specific conductance and the reading of the mA meter is set exactly at the 0-line for the saturation point, usually 70 mA. This is the zero conductivity to be used for the pan control.

The sensitive point is the temperature control in testing the specific conductance of the raw material. For this can be used at the pan floor a very simple water-bath with thermometer filled with cold water as well as with condensate. It is possible to make such an arrangement that the deter-

mination of the specific conductance is done directly on the pan floor. It is also possible that the specific conductance is determined in the laboratory, if we know exactly the capacity of the pan electrodes.

In the conductivity control is usually used an mA meter with a scale going from 0–100 mA. The saturation point is set via a voltage regulator at exactly 70 mA. When this is done it is possible to use exactly the same conductivity values for the different boilings independent of variations in the ash % nonsugars of the materials to be crystallized. The best results are obtained with the conductivity control if all the electrodes in the pans are standardized and constructed in such a way that they have all the same capacity.

The investigations on the relationship between conductivity and sugar saturation have given us a solid foundation for the determination of the supersaturation based only on electrical conductivity. It is possible to express supersaturations in conductivity values.

13. Supersaturation in Technical Sugar Crystallization

Although the expression 'supersaturation' is used frequently in technical publications, the number of actual determinations of the supersaturation under the conditions of the crystallization process is extremely limited. The main reason is that the determination of the supersaturation is difficult and time consuming. The customary definition of supersaturation is

$$\text{supersaturation} = \frac{\text{sucrose in solution of purity } P \text{ at temperature } T \% \text{ water}}{\text{sucrose in solution of purity } P \text{ at temp. } T \text{ at saturation point } \% \text{ water}}$$

what is usually written as

$$\text{supersaturation} = \frac{\text{brix of solution of purity } P \text{ at temperature } T \% \text{ water}}{\text{brix of solution of purity } P \text{ at temp. } T \text{ at saturation point } \% \text{ water}}$$

The difficulty in the application of this formula is that we are using brix and water. For technical investigations we can use as brix: true solids, hydrometer brix determined after a dilution 1 : 1, or the refractometric brix.

The simplest is the determination of the refractometric brix; however, it must be understood that the refractometric brix is not the same as true solids. For low purity products the true solids are always lower than the refractometric brix. The difference f.i. for molasses of 40 gravity purity can be 2 to 4 brix between the two values.

Much greater is the difference between the brix determined by hydro-

meter after dilution 1 : 1 and true solids. For low purity canesugar products as f.i. molasses this difference can be as high as 10 points.

The determination of a large number of true solids contents in low purity products is cumbersome and requires special precautions in the determination of dry solids (drying at low temperature under vacuum) to avoid decomposition during the water analysis.

For cane juices a very elaborate study has been made on the relationship between purity, temperature, brix, saturation and supersaturation by THIEME in Java.⁹ The results of THIEME have been checked by the Java

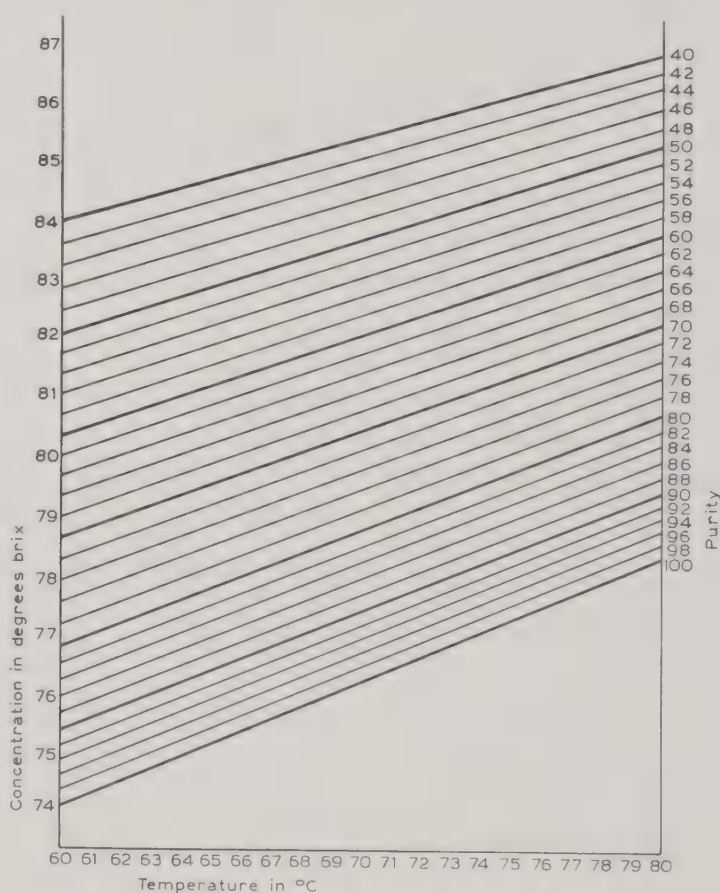


Fig. 9/14. Relationship for cane juices between brix, temperature in °C and purity at saturation point, according to THIEME.

Sugar Experiment Station using the refractometric brix as brix value. It must be understood that these Java studies are based on the nonsugar composition which is substantially different in other cane producing areas. The canesugar products investigated by THIEME and the Java Sugar Experiment Station had a nonsugar composition approximately as

follows: sulfated ash % true nonsugars (true solids — sucrose) 23–27%, reducing sugars 37–43%, organic nonsugars 30–40%.

The tables on supersaturation and boiling house studies used in Java publications must always be considered with this nonsugar composition in mind. For other countries and for other nonsugar compositions these

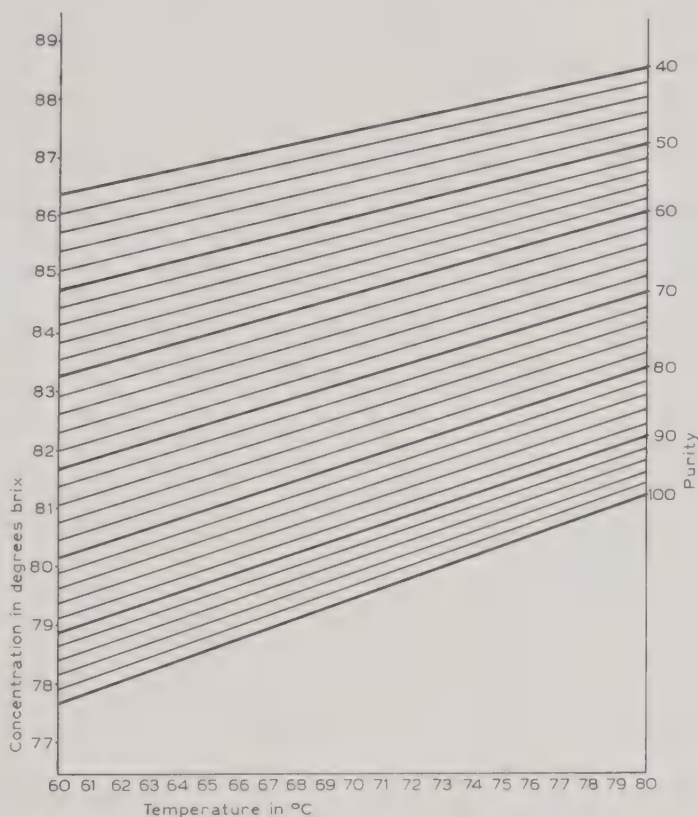


Fig. 9/15. Relationship for cane juices of brix, temperature in °C and purity for the supersaturation of 1.20, according to THIEME.

tables must be verified and perhaps be adjusted because the solubility of sucrose which the saturation tables stand for is determined especially for products of lower purities by the nonsugar composition.

Just as the solubility tables for the beetsugar industry in Chapter 12 taken from the fundamental studies by GRUT have no applicability for cane-sugar products, so it is also possible that the Java tables must be revised for other cane areas or special mills where an abnormal nonsugar composition exists.

In Figs. 9/14 and 9/15, we give the Java tables, for saturated cane juices, the relationship between refractometric brix, purity and temperature in °C, and a similar graph for the supersaturation at 1.20.

TABLE 5

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SATURATED CANESUGAR PRODUCTS

Temp. °C	Purity								
	92	90	88	86	84	82	80	78	76
61	75.4	75.7	76.0	76.3	76.6	76.8	77.1	77.5	77.8
62	75.6	75.9	76.2	76.5	76.7	77.0	77.3	77.6	78.0
63	75.8	76.1	76.4	76.6	76.9	77.2	77.5	77.8	78.2
64	76.0	76.3	76.5	76.8	77.1	77.4	77.7	78.0	78.4
65	76.2	76.5	76.7	77.0	77.3	77.6	77.9	78.2	78.6
66	76.4	76.6	77.0	77.2	77.5	77.8	78.1	78.4	78.7
67	76.6	76.9	77.1	77.4	77.7	78.0	78.3	78.6	78.9
68	76.8	77.1	77.3	77.6	77.9	78.2	78.5	78.8	79.1
69	77.0	77.3	77.5	77.8	78.1	78.4	78.7	79.0	79.3
70	77.2	77.5	77.7	78.0	78.3	78.6	78.9	79.2	79.5
71	77.4	77.7	77.9	78.2	78.5	78.8	79.0	79.3	79.6
72	77.6	77.9	78.1	78.4	78.7	79.0	79.2	79.5	79.8
73	77.8	78.1	78.3	78.6	78.9	79.2	79.4	79.7	80.0
74	78.0	78.3	78.5	78.8	79.1	79.4	79.6	79.9	80.2
75	78.2	78.5	78.7	79.0	79.3	79.5	79.8	80.1	80.4
76	78.4	78.7	78.9	79.2	79.5	79.7	80.0	80.3	80.6
77	78.7	78.9	79.1	79.4	79.7	79.9	80.2	80.5	80.8
78	78.9	79.1	79.3	79.6	79.9	80.1	80.4	80.7	81.0
79	79.1	79.3	79.5	79.8	80.1	80.4	80.6	80.9	81.2
80	79.3	79.5	79.7	80.0	80.3	80.5	80.8	81.1	81.4

The Java data published by THIEME and verified by the Java Sugar Experiment Station were for the Java sugar industry a reliable foundation to determine the supersaturation during the boiling process.

It is customary to use Tables 5,6,7,8,9 and 10 by determining the refractometric brix, as a sugar refractometer is calibrated directly in °sucrose or °brix, and to express the concentration of the solution tested per 100 water. For instance, a sugar solution of a purity 78 at 63° C has a refractometric brix of 82.5. What is the supersaturation of this solution? 82.5 brix equals 471 brix per 100 water. According to the tables the saturation brix at 78 purity and 63° C is 77.8, corresponding with 350 brix per 100 water. The supersaturation of this solution is $\frac{471}{350} = 1.35$.

These are the values reported in boiling house studies and crystallization experiments.

TABLE 5 (CONTINUED)

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SATURATED CANESUGAR PRODUCTS.

Temp. °C	74	72	70	Purity		64	62	60	58
				68	66				
51	78.2	78.5	78.9	79.2	79.6	79.9	80.3	80.6	80.9
52	78.3	78.7	79.0	79.3	79.7	80.1	80.4	80.8	81.1
53	78.5	78.9	79.2	79.6	79.9	80.3	80.6	81.0	81.3
54	78.7	79.0	79.4	79.7	80.1	80.4	80.8	81.1	81.4
55	78.9	79.3	79.6	79.9	80.2	80.6	80.9	81.3	81.6
56	79.1	79.4	79.7	80.1	80.4	80.8	81.1	81.4	81.7
57	79.3	79.6	79.9	80.3	80.6	80.9	81.3	81.6	81.9
58	79.4	79.8	80.1	80.4	80.8	81.1	81.5	81.8	82.1
59	79.6	79.9	80.3	80.6	80.9	81.3	81.6	81.9	82.2
60	79.8	80.1	80.5	80.8	81.1	81.4	81.7	82.1	82.4
61	80.0	80.3	80.6	80.9	81.3	81.6	82.0	82.3	82.6
62	80.2	80.5	80.8	81.1	81.5	81.8	82.1	82.4	82.7
63	80.3	80.7	81.0	81.3	81.7	82.0	82.3	82.6	82.9
64	80.5	80.9	81.2	81.5	81.8	82.2	82.5	82.8	83.1
65	80.7	81.1	81.4	81.7	82.0	82.3	82.7	83.0	83.3
66	80.9	81.2	81.6	81.9	82.2	82.5	82.8	83.1	83.4
67	81.1	81.4	81.8	82.1	82.4	82.7	83.0	83.3	83.6
68	81.3	81.6	81.9	82.2	82.6	82.9	83.2	83.5	83.8
69	81.5	81.8	82.1	82.4	82.7	83.0	83.4	83.7	83.9
70	81.7	82.0	82.3	82.6	82.9	83.2	83.5	83.8	84.1

14. Technical Control Instrument for Conductivity Control

The apparatus for conductivity control consists of a transformer to reduce the AC voltage of the factory to a low voltage that can vary between 4 and 30 V, an mA recording or indicating meter with a range of 0–100 mA and internal resistance of approximately 100 Ω , and a set of electrodes inserted in the vacuum pan and located in such a way that the crystallizing masse-cuite flows uninterrupted between the electrodes without interference of vapor bubbles enabling the conductivity of the masse-cuite to be actually measured.

The first technically complete apparatus for conductivity control was constructed in Hengelo, the Netherlands, by the HEEMAF (Hengelosche Electriche en Mechanische Apparatenfabriek). In Figs. 9/16 and 9/17 we give a picture of this apparatus as it has been installed in many sugar pro-

TABLE 5 (CONTINUED)

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SATURATED CANESUGAR PRODUCTS.

Temp. °C	56	54	52	50	Purity 48	46	44	42	40
61	81.3	81.6	81.9	82.3	82.7	83.0	83.4	83.8	84.2
62	81.4	81.7	82.1	82.4	82.8	83.2	83.5	83.9	84.3
63	81.6	81.9	82.2	82.6	83.0	83.3	83.7	84.0	84.5
64	81.7	82.1	82.4	82.7	83.1	83.5	83.8	84.2	84.6
65	81.9	82.2	82.5	82.9	83.3	83.6	84.0	84.3	84.7
66	82.0	82.4	82.7	83.0	83.4	83.8	84.1	84.5	84.9
67	82.2	82.5	82.9	83.2	83.6	83.9	84.3	84.6	85.1
68	82.4	82.7	83.0	83.4	83.7	84.1	84.4	84.8	85.2
69	82.5	82.8	83.2	83.5	83.8	84.2	84.6	84.9	85.3
70	82.7	83.0	83.3	83.7	84.1	84.4	84.7	85.1	85.4
71	82.9	83.2	83.5	83.8	84.2	84.5	84.9	85.2	85.6
72	83.0	83.3	83.7	84.0	84.3	84.7	85.0	85.4	85.7
73	83.2	83.5	83.8	84.1	84.5	84.8	85.2	85.5	85.9
74	83.4	83.7	84.0	84.3	84.6	85.0	85.3	85.6	86.0
75	83.6	83.9	84.1	84.5	84.8	85.1	85.5	85.8	86.1
76	83.7	84.0	84.3	84.6	85.0	85.3	85.6	85.9	86.3
77	83.9	84.2	84.5	84.8	85.1	85.4	85.8	86.1	86.4
78	84.1	84.4	84.7	85.0	85.3	85.6	85.9	86.2	86.5
79	84.2	84.5	84.8	85.1	85.4	85.7	86.0	86.3	86.7
80	84.4	84.7	85.0	85.3	85.6	85.9	86.2	86.5	86.8

ducing areas and beetsugar factories as well as canesugar factories and refineries.

This instrument has also been made by other equipment manufacturing companies. The total number of conductivity control instruments installed over the whole world is approximately 800.

15. The Evaporating Surface in Vacuum Pans

The evaporating or heating surface in vacuum pans is usually expressed in sq. ft or sq. m. The capacity of this heat transfer area is usually expressed in the amount of vapor or steam conducted per hour which is usually considered equal to the amount of water evaporated from the massecuite.

The evaporation rate of massecuites is variable during the boiling process depending on the volume of massecuite in the pan and the system of

TABLE 6

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SUPERSATURATED SUGAR SOLUTIONS WITH A SUPERSATURATION OF 1.20.

Temp. °C	92	90	88	Purity		82	80	78	76
				86	84				
61	78.6	78.9	79.1	79.4	79.7	79.9	80.2	80.5	80.8
62	78.8	79.1	79.3	79.6	79.8	80.1	80.4	80.7	81.0
63	79.0	79.2	79.5	79.8	80.0	80.3	80.5	80.8	81.1
64	79.2	79.4	79.7	79.9	80.2	80.4	80.7	81.0	81.3
65	79.4	79.6	79.8	80.1	80.4	80.6	80.9	81.2	81.5
66	79.5	79.8	80.0	80.3	80.5	80.7	81.0	81.3	81.6
67	79.7	79.9	80.2	80.5	80.8	81.0	81.2	81.5	81.8
68	79.9	80.1	80.4	80.6	80.9	81.1	81.4	81.7	82.0
69	80.1	80.3	80.5	80.8	81.0	81.3	81.5	81.8	82.1
70	80.2	80.5	80.7	81.0	81.2	81.5	81.7	82.0	82.3
71	80.4	80.7	80.9	81.2	81.4	81.6	81.9	82.2	82.5
72	80.6	80.8	81.1	81.3	81.6	81.8	82.1	82.3	82.6
73	80.8	81.0	81.3	81.5	81.8	82.0	82.2	82.5	82.8
74	81.0	81.2	81.5	81.7	81.9	82.2	82.4	82.7	83.0
75	81.2	81.4	81.6	81.9	82.1	82.4	82.6	82.9	83.1
76	81.4	81.6	81.8	82.1	82.3	82.5	82.7	83.0	83.3
77	81.5	81.8	82.0	82.2	82.5	82.7	82.9	83.2	83.5
78	81.7	82.0	82.2	82.4	82.6	82.9	83.1	83.4	83.7
79	81.9	82.1	82.4	82.6	82.8	83.1	83.3	83.6	83.8
80	82.1	82.3	82.6	82.8	83.0	83.3	83.5	83.7	84.0

boiling. The evaporation rate or steam consumption of many vacuum pans has been measured via recording water meters built in the condensate line. We found the following data for the evaporation rate per sq.m. surface for a coil pan using exhaust steam with a pressure of 1.3 to 1.4 kg/cm² abs. (Table 7).

TABLE 7

CONDENSATION CAPACITY IN LITERS OF CONDENSATE/M²/H IN COIL PAN FOR A-MASSECUITE (PURITY 86). (VAPOR PRESSURE 1.3-1.4 KG/CM² ABS)

Concentrating syrup of 60 brix to saturation	70-120
Feeding with magma and maturing of seed	58-70
Boiling of strike from footing to final massecuite volume	47-58
Finishing of strike during last 20 min of boiling	23-47

It can be observed that the evaporation rate decreases with an increase

TABLE 6 (CONTINUED)

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SUPERSATURATED SUGAR SOLUTIONS WITH A SUPERSATURATION OF 1.20.

Temp. °C	74	72	70	68	Purity 66	64	62	60	58
61	81.1	81.4	81.7	82.0	82.4	82.7	83.0	83.3	83.6
62	81.3	81.6	81.9	82.2	82.5	82.8	83.2	83.5	83.8
63	81.4	81.7	82.0	82.4	82.7	83.0	83.3	83.6	83.9
64	81.6	81.9	82.2	82.5	82.8	83.2	83.5	83.8	84.0
65	81.8	82.1	82.4	82.7	83.0	83.3	83.6	83.9	84.2
66	81.9	82.2	82.5	82.8	83.1	83.5	83.8	84.1	84.4
67	82.1	82.4	82.7	83.0	83.3	83.6	83.9	84.2	84.5
68	82.3	82.6	82.9	83.2	83.5	83.8	84.0	84.3	84.6
69	82.4	82.7	83.0	83.3	83.6	83.9	84.2	84.5	84.8
70	82.6	82.9	83.2	83.5	83.8	84.1	84.4	84.6	84.9
71	82.8	83.1	83.3	83.6	83.9	84.2	84.5	84.8	85.1
72	82.9	83.2	83.5	83.8	84.1	84.4	84.7	84.9	85.2
73	83.1	83.4	83.7	84.0	84.3	84.5	84.8	85.1	85.4
74	83.3	83.5	83.8	84.1	84.4	84.7	85.0	85.3	85.5
75	83.4	83.7	84.0	84.3	84.6	84.9	85.1	85.4	85.6
76	83.6	83.9	84.1	84.4	84.7	85.0	85.3	85.6	85.8
77	83.8	84.0	84.3	84.6	84.9	85.2	85.4	85.7	85.9
78	84.0	84.2	84.5	84.8	85.1	85.3	85.6	85.9	86.1
79	84.1	84.4	84.6	84.9	85.2	85.5	85.7	86.0	86.3
80	84.3	84.5	84.8	85.1	85.4	85.6	85.9	86.2	86.4

of the concentration of the massecuite and with the height of the massecuite in the pan.

In a 7-coil pan the evaporation rate of the individual pans was determined during the last phase of the boiling process when the whole pan reached its final net volume of massecuite giving the following data:

TABLE 8

CONDENSATION CAPACITY IN LITERS OF CONDENSATE/M²/H FOR DIFFERENT COILS IN COIL PAN DURING LAST 20 MINUTES OF BOILING

Lowest coil (bottom coil)	23
2nd coil	25
3rd coil	33
4th coil	44
5th coil	38*
6th coil	55
7th coil (upper coil)	61

* Imperfect functioning of removal of non-condensable gases.

TABLE 6 (CONTINUED)

CONCENTRATION IN °BRIX, PURITY, AND TEMPERATURE IN °C FOR SUPERSATURATED SUGAR SOLUTIONS WITH A SUPERSATURATION OF 1.20.

Temp. °C	56	54	52	50	Purity 48	46	44	42	40
51	83.9	84.2	84.5	84.8	85.1	85.4	85.7	86.1	86.5
52	84.1	84.4	84.6	84.9	85.2	85.5	85.9	86.2	86.6
53	84.2	84.5	84.8	85.1	85.4	85.7	86.0	86.3	86.8
54	84.3	84.6	84.9	85.2	85.5	85.8	86.1	86.4	86.9
55	84.5	84.8	85.0	85.3	85.6	85.9	86.4	86.6	87.0
56	84.6	84.9	85.2	85.5	85.8	86.1	86.4	86.7	87.1
57	84.8	85.0	85.3	85.6	85.9	86.2	86.5	86.8	87.2
58	84.9	85.2	85.5	85.7	86.0	86.3	86.6	86.9	87.3
59	85.1	85.3	85.6	85.9	86.2	86.5	86.8	87.1	87.4
60	85.2	85.5	85.7	86.0	86.3	86.6	86.9	87.2	87.6
61	85.4	85.6	85.9	86.2	86.4	86.7	87.0	87.3	87.7
62	85.5	85.8	86.0	86.3	86.6	86.9	87.2	87.5	87.8
63	85.6	85.9	86.2	86.4	86.7	87.0	87.3	87.6	87.9
64	85.8	86.0	86.3	86.5	86.8	87.1	87.4	87.7	88.0
65	85.9	86.2	86.4	86.7	87.0	87.3	87.6	87.8	88.1
66	86.1	86.3	86.6	86.8	87.1	87.4	87.7	88.0	88.3
67	86.2	86.5	86.7	87.0	87.2	87.5	87.8	88.1	88.4
68	86.4	86.7	86.9	87.1	87.4	87.7	87.9	88.2	88.5
69	86.5	86.7	87.0	87.2	87.5	87.8	88.1	88.4	88.6
70	86.7	86.9	87.2	87.4	87.7	88.0	88.2	88.5	88.7

The rate of evaporation in the individual coils varies considerably with the height of the coil in the pan.

In old-fashioned pans constructed with a so-called double bottom and suitable for evaporation, it was found that the double bottom in vacuum pans under no condition was giving a higher evaporation rate than 30 l/m²/h with a steam pressure of 1.5 kg/cm² abs. The average value found was approximately 12 l/m²/h. A part of the formed condensate will undoubtedly result from the loss of heat via radiation of the bottom. The contribution of the double bottom to evaporation in vacuum pans is according to our opinion negligible.

16. Technological Investigations on the Crystallization Process

Technological studies on the crystallization process under factory condi-

tions are rather complicated and time-consuming. If it is the intention of the factory staff to make such special investigations, which are of great educational value to the factory staff, it is necessary that a chemist or technologist be able to devote full time to this study and be assisted by someone to collect samples, to make the necessary analyses and to record the essential

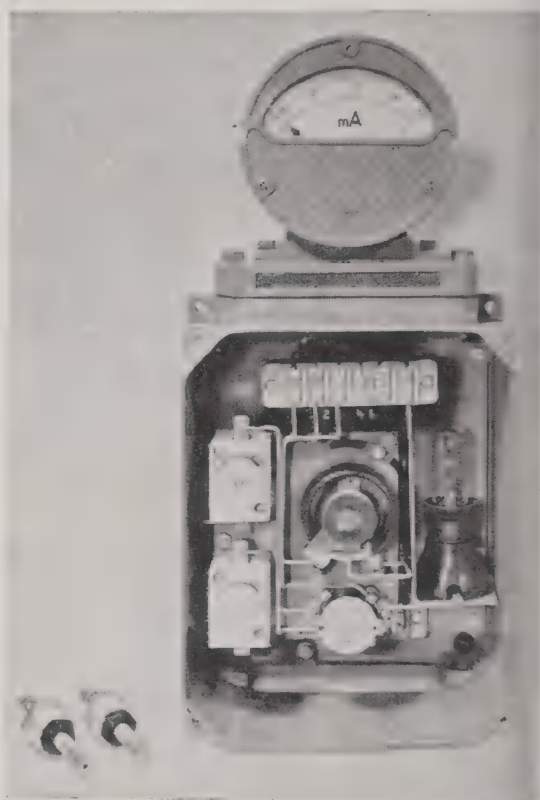
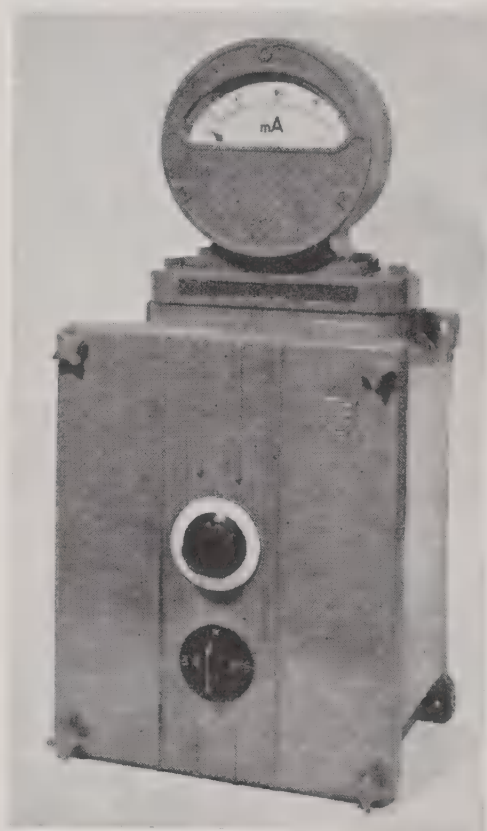


Fig. 9/16. Conductivity control instrument as manufactured by HEEMAF, Hengelo, Holland.

Fig. 9/17. Inside view of the conductivity control instrument as manufactured by HEEMAF, Hengelo, Holland, showing the voltage regulator, the voltage stabilizer and the electrodes to be mounted in the pan for measuring the conductivity.

data for the history of a complete boiling. This study can practically never include the determination of all essential data without recording instruments. Regarding the pan and the boiling process in this pan the following must be recorded:

(a) Temperature of the massecuite. It is recommendable to make two temperature determinations, one of the massecuite below the heating elements before entering the tubes of the calandria, the second temperature of the massecuite 40 to 50 cm above the calandria.

- (b) Pressure of the vapor or steam entering the calandria.
- (c) Vacuum during the boiling process.
- (d) Electrical conductivity of the massecuite with the electrodes set in the bottom of the pan but at a distance from the pan wall of at least 4".

During the crystallization process the following must be recorded:

- (a) Manipulations of the pan boiler as to feeding the pan; manipulations of the feed valves; volume of materials fed to the pan.
- (b) Adjustments of the vapor or steam inlet valve.
- (c) Volume of massecuite in the pan.
- (d) Special manipulations as intake of water in the pan.
- (e) The exact times when a pan is charged and discharged as well as the times for the beginning and end of the different phases of the crystallization process.
- (f) Periodic samples of the massecuite must be taken for analysis on the refractometric brix of the mother liquor and periodically larger samples to be centrifuged in a laboratory centrifugal to determine the purity of the mother liquor to calculate the crystal content of the massecuite.
- (g) Samples must be taken for the complete analysis of the raw materials used in the crystallization experiment and of the finished strike with centrifuging a part of this sample of the massecuite to determine the crystal yield via the analysis of the molasses and massecuite.

It is possible by such a systematic investigation to discover the imperfections in the used crystallization technique, respectively imperfections in the existing operational conditions as far as vapor pressure, regularity of vacuum, rate of evaporation, etc. are concerned.

Our experience is that in many sugar factories it is possible to increase substantially the capacity of a vacuum pan only by improvements in the operational conditions. The two most important factors for efficient pan performances are a constant pressure of the steam, continuous feeding of pans to maintain a constant evaporation rate in the pans, and a constant but adjustable vacuum.

Many arguments in the sugar industry regarding too small capacity of a pan station for which a solution is found in installing more units, show that after a thorough investigation of the crystallization process there is no justification whatever to increase the number of pans. The simplest and most economic solution must be found primarily in an absolute control of operational conditions. In Table 9, we give an example of the boiling of an *A*-massecuite of a purity of 82 boiled by the master boiler of a Java sugar factory in an old-fashioned small coil pan of 140 hl. As magma

a mixture of *C*-sugar and syrup was used. The boiling started with the master boiler feeding the pan with 50 hl concentrated syrup. After that 15 hl of magma was introduced resulting that the master boiler had estimated the saturation of the syrup in the pan inaccurately causing nearly all the *C*-sugar to be dissolved. The footing should have been concentrated to a higher degree of saturation, after which a second 15 hl of magma is introduced. The supersaturation was calculated via refractometric brix using

TABLE 9

RECORDED DATA OF BOILING *A*-MASSECUITE ON A FOOTING OF SYRUP AND *C*-SUGAR MAGMA IN A COIL PAN. PURITY OF MASSECUITE 84

Time	Vol. of massec. hl	Vac. cm Hg	Temp. of massec. °C	Cond. mA	Massec. brix	Mother liquor brix	Crystal content of massec. %	Super-saturation	Manipulations of pan boiler
0 min.	0	69		105					Intake of syrup, concentrated, feeding 15 hl <i>C</i> -sugar magma.
5 min.	65	69.5	48.6	100					Intake magma finished.
10 min.		69.0	51.0	97	75.6		0		
18 min.	60	68.6		90					Second intake of 15 hl <i>C</i> -sugar magma (<i>C</i> -sugar size 0.3 mm linear).
20 min.	75	68.8	52.0	80	79.0	76.0	12.5	1.00	End of magma intake, concentrating, no feeding of pan.
30 min.		69.5	49.8	65					
40 min.		69.8	52.0	65	83.2	78.5	21.7	1.07	
50 min.		68.0	55.8	61					
1 h.		67.5	58.0	58		79.0			
1 h. 10 min.		67.0	59.6	57					
1 h. 20 min.	64	67.5	59.6	51	89.2	79.4	47.5	1.09	Started feeding of pan with syrup, continuous feeding.
1 h. 30 min.		68.2	57.0	59					
1 h. 40 min.		68.0	57.7	59					
1 h. 50 min.	83	68.0	57.5	62	89.5	80.0	47.5	1.08	
2 h.		68.0	57.5	61					
2 h. 10 min.		68.0	57.6	61					
2 h. 20 min.		67.2	59.0	58	89.8	80.5	47.7	1.12	
2 h. 30 min.		67.4	59.0	56					
2 h. 40 min.		67.4	58.4	57					
2 h. 50 min.		67.4	58.4	56					
3 h.		67.6	58.8	54	90.2	79.6	52.0	1.04	
3 h. 10 min.	135	68.2	57.4	53					End of feeding of pan with syrup; finishing of strike by intake of movement water.
3 h. 20 min.	130	68.8	57.0	50	91.0	79.0	57.0	1.02	Strike finished and discharged from pan to crystallizer (grain size 0.9 mm linear).

the saturation tables by THIEME given in the preceding paragraph as Table 6. In Fig. 9/18 we have represented graphically the history of this boiling. The recorded temperature is the temperature measured above the heating elements. This gives us the lowest supersaturation value of the massecuite.

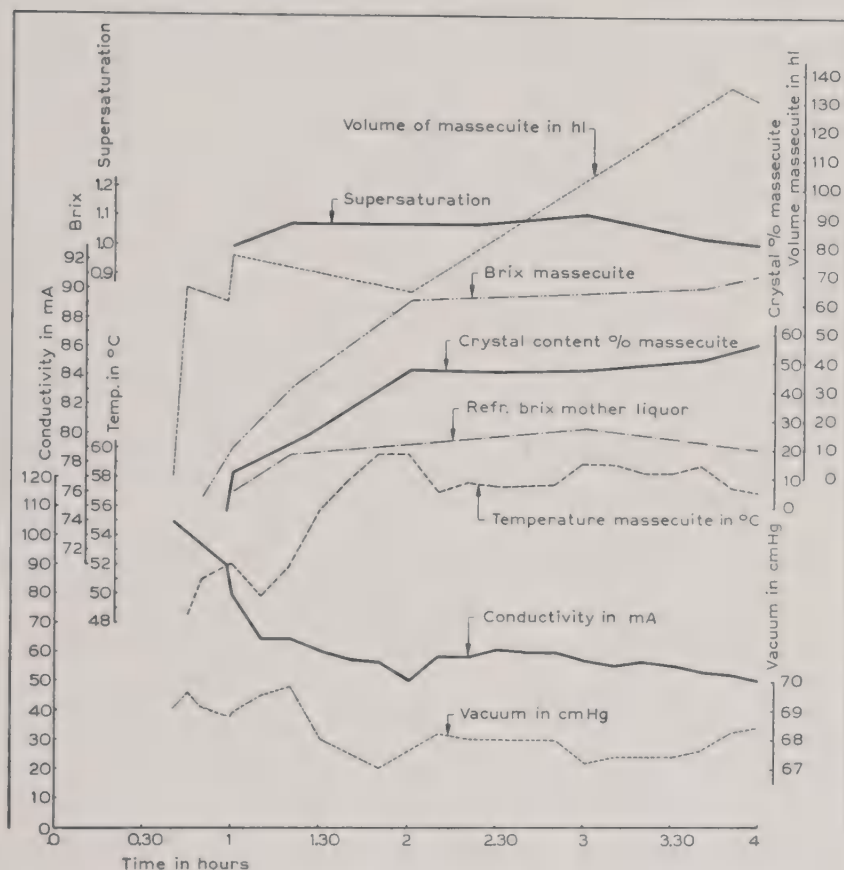


Fig. 9/18. Complete recording of operational conditions of the crystallization of an A-boiling in a cane sugar factory (Table 9).

These studies have been made with all kinds of boiling and pans of various designs.¹⁰ They have given us the foundation for the recommended construction as outlined in the preceding paragraphs and the guiding principles for the different phases of the crystallization process. They show the practical results which can be obtained under the best operational conditions realizable in every modern sugar factory today.

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CHAPTER 10

EVAPORATION AND CIRCULATION IN THE CRYSTALLIZATION PROCESS

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1. Introduction

The object of the crystallization process is to grow crystals from a sugar solution from which water is simultaneously removed by evaporation. This process is one step more complicated than evaporation in an effect. In the process of crystallization, there occurs simultaneously transfer of mass and heat between three interacting phases. Often the rate of evaporation has to be controlled to fit the rate of crystallization. While the possible limit of allowable temperature differentials is fairly wide – we must, of course, avoid using so high a temperature as to burn the material – the possible range of supersaturation is much narrower. If the supersaturation is raised too high, new crystal nuclei appear and this leads to the establishment of false grain. If, on the other hand, the solution became locally unsaturated, the crystals there commence to dissolve and the resultant erosion of the surface has serious effects. Attainment of the correct control of the supersaturation is complicated by the fact that at a given concentration, the degree of supersaturation falls with rising temperature. A pan may exhibit a fairly uniform concentration but any local hot spot due to sluggish movement or high local heat transfer rates may give rise to a locally unsaturated patch. Rapid and even flow of heat to the vapor and from the growing sucrose crystals gives rise to small temperature and supersaturation differentials. Both these differences may be reduced by circulation of the fluid which process tends to bring new liquid into contact with the growing crystal faces and with the heating surface. The former type of contact tends to increase the rate of crystallization by reducing the thickness of the stagnant layer around each crystal face. The latter type tends to increase the rate of heat transfer by correspondingly reducing the thickness of the stagnant layer around the heating surface.

The complicated kinetic changes going on inside an evaporator and crystallizer may perhaps best be summarized by postulating the occurrence of three simultaneous and inter-acting processes, namely:

- (1) the flow of heat and mass to the vapor bubbles;
- (2) the flow of mass to, and heat from, the surfaces of the growing crystals;
- (3) the mechanical movement or circulation of the fluid parts of the assembly with the associated tendency to sweep along small solid particles, *i.e.* the crystals, with the fluid.

Each one of these flow processes may be regarded as taking place at a definite rate determined jointly by an externally maintained driving force for that process and an internal resistance opposing the driving forces.

2. Effective Driving Forces

The driving force for a heat flow is always a temperature difference. The property which acts as the driving force for a mass flow is a little more difficult to define although easy definitions are possible in certain special cases. Thus for mass transport in gaseous systems the pressure – or in the case of transport of one particular chemical substance through others, the partial pressure – is the measure of the driving force. In homogeneous liquid systems the concentration may be used as a measure of the driving force. In systems involving two chemical phases, *e.g.* solid – liquid or liquid – vapor; neither the concentration nor the partial pressure is an appropriate measure. We may, however, use such properties as the difference in partial pressure in the gas phase and that partial pressure which is in equilibrium with the concentration attained in the liquid phase; or the difference between the concentration in the liquid phase and the concentration in equilibrium with the same component in the other phase. This departure in the measure of some appropriate property in one phase from the state of equilibrium with the other phase is measured by the thermodynamical property known as the activity.

(a) *Evaporation*

In the process of evaporation heat is transferred from the heating surface to the liquid while vapor molecules are transferred from the liquid solution to growing bubbles.

For a liquid solution maintained at a constant pressure and concentration, the boiling point remains constant. Consequently heat flowing into the liquid will produce growing and expanding bubbles of vapor while the

temperature remains constant. Consequently the driving force for heat flow is the temperature excess of the heated surface over and above the (local) boiling point of the liquid. This temperature difference will be less than the temperature excess of the steam supplied to heating coils or calandria over that of the boiling point by the amount of the temperature drop across the steam-side film and the walls of the heating surface.

The driving force for the mass transfer of water vapor from syrup to growing bubbles is measured by the difference in the thermodynamical activity of water in the syrup and vapor phase respectively.

(b) *Crystallization*

This process is accompanied both by the transference of mass to the growing crystal surface and the liberation of the heat of crystallization at that surface. The factor controlling the rate of crystallization is the degree of supersaturation or more accurately the difference in thermodynamical activity between the sucrose actually in solution and that in equilibrium with the solid surface – *i.e.* that at the saturation concentration. The supersaturation, or ratio of the actual concentration to the saturation concentration, varies with both the concentration and the temperature. In particular the effective degree of supersaturation may be less near the crystal surface than in the bulk of liquid even under iso-thermal conditions. When the crystal is growing steadily sucrose molecules are flowing in a steady stream from the bulk of the liquid to the crystal surface. This steady flow causes a depletion of the solution in the immediate vicinity of the crystal faces. The concentration of the solution near the crystal can only be maintained by diffusion of sucrose molecules from more distant parts of the solution and is thus less near the crystal faces than in the bulk of the liquid. This deficiency in the solution concentration near the crystal face becomes the more pronounced the faster the crystal grows.

There is also another factor which adversely affects the supersaturation near the face of a growing crystal. The formation of crystal involves the evolution of heat. Some figures for the heat of crystallization, which is equal and opposite to the heat of solution, have been collected by LYLE¹ who shows that the heat of crystallization may amount to $2\frac{1}{2}\%$ of the latent heat for the evaporation of steam.

This heat liberated at the crystal surface by the act of crystallization tends to raise the local temperature and thus further to decrease the local supersaturation.

(c) *Circulation*

Circulation in the pan, unless maintained by mechanical drive, is the result of the hydrostatic head difference produced by the difference in density between the ascending heated foam of liquor and vapor bubbles produced by the heating surface and the cooler descending column of liquor from which those bubbles have escaped.

The immediate cause of circulation is this hydrostatic head difference. The head difference in turn is the result of the feeding of heat into one part of the pan and not into another. However, there are other ways of increasing the hydrostatic head difference. Rate of circulation for example may be increased by injecting live steam below the lowest heating surface. FITZWILLIAM and YEARWOOD² have advocated this method of steam injection for increasing pan circulation claiming that the escaping bubbles of steam, by expanding as they rise through the heated zone, produce a severe stirring effect.

The use of mechanical fans or paddles to increase circulation has been advocated by WEBRE^{3, 4} who introduced a single motor-driven screw impeller at the bottom of the vessel to augment natural circulation. He claims improved control with this instrument. However, not all authorities on sugar technology have agreed with the claim that natural circulation, in a properly designed vacuum pan, is inadequate. The WEBRE impeller certainly consumes considerable power.

3. Effective Resistances

The various driving forces tending to produce a flow of heat, chemical matter and mechanical circulation are opposed by resistances due to the internal structure and properties of the assemblies concerned. A knowledge of these resistances will permit an estimate of the flow rates produced by a given driving force.

A characteristic of the systems involved in evaporation and crystallization, and one indeed common to many chemical engineering operations, is that the different flow processes are interconnected, or coupled, so that a change in the flow of any one process produces a modification of the resistances associated with the flow of the other processes. The theoretical treatment of systems of this nature is still in its infancy. A review of such progress as has been made will be found in ref. ⁵.

(a) *Evaporation*

The resistance per unit area to the process of heat flow is the reciprocal of the liquid side film coefficient. The liquid side film coefficient may be increased, and the resistance decreased, by any of the factors which decrease the thickness of the stagnant film around the heated surfaces. Prominent among these factors are the overall temperature difference and the velocity of circulation.

If L is taken as the latent heat of evaporation of water at the operating temperature then for every L units of heat which pass through the heating surface into the massecuite one unit of water vapor must pass from the liquid to the gaseous phase. Heat flow and mass flow in evaporation are thus coupled in the sense indicated above and, furthermore, coupled in a particularly rigid manner. Any mechanism which suppresses the formation of vapor must necessarily also suppress the flow of heat into the liquid. This can only be done by reducing the effective driving force for heat flow, *i.e.* by increasing the temperature of the zone of liquid in immediate contact with the heating surface. Any suppression of vapor formation thus results in superheating of the massecuite near the heating coils or calandria.

(b) *Crystallization*

There are at least three important factors which limit the rate at which a crystal can grow when placed in a solution of known driving force for mass transfer to the crystal surface – *i.e.* in a solution of known supersaturation. These three factors correspond to three separate resistances opposing the growth of crystals. In turn they are:

- (α) The factors limiting the rate of growth of crystal when molecules of sucrose are supplied to the surface at an ample rate.
- (β) The fact that the act of building up the crystal will rob the solution in its immediate vicinity of solute (or sucrose) molecules. This depletion of the solution can only be made good by diffusion so that a film of lower concentration is built up around the growing crystal.
- (γ) The heat of crystallization liberated at the crystal surface tends to increase the temperature of the film so that its degree of supersaturation falls even more than its concentration. Transport of heat is the only factor which can oppose this raising of the film temperature.

Resistance factors (α) are those associated with the intrinsic rate of growth of sucrose in pure solutions kept particularly well stirred. As such these factors have been treated in Chapter 4.

Resistance factors (β) are determined by the thickness of the stagnant layer around the growing crystal and by the rate of diffusion of sucrose through that layer. This rate of diffusion, in turn, is inversely correlated with the viscosity of the liquid in the stagnant layer. The presence of impurities in solution may adversely affect the rate of diffusion and increase the resistance to crystal growth so that the rate of crystallization for a given degree of supersaturation may be much lower in an impure than in a pure solution. Impurities in solution not only get in the way and thus impede the diffusion of sucrose molecules but also their presence may increase the thickness of the film of low concentration around the crystal faces. This effect may be particularly pronounced if the impurities are of such a nature as to increase the viscosity of the solution. A number of authorities, prominent among them COALSTAD⁶, have suggested that the surface activity of impurities also plays a dominant role in this respect. Such a property, he claims, permits the impurity to compete with sucrose molecules for space on the growing crystal face. A general review of the rates of crystal growth in low grade massecuites has been given by MCGINNIS, MOORE and ALSTON⁷.

Resistance factor (γ) represents a process of the flow of heat which is coupled to the flow of mass. Any restriction to the flow of heat will produce an unfavorable change in the effective degree of supersaturation at the crystal face while any factor which increases the rate of removal of heat from the crystal face will increase the rate of growth of the crystal.

(c) *Circulation*

The resistance offered to circulation is of a purely mechanical nature and is perhaps relatively easier to discuss than the resistances offered to heat and mass flow in evaporation and crystallization. The two factors concerned in determining the resistance to circulation are the drag produced by the shape and nature of the pan and the viscosity of the massecuite to be treated.

The path of the circulating massecuite in the pan is necessarily obstructed by the heating surfaces, whether in the form of coils or calandria, by feed pipes and any control instruments. To understand the nature of resistance to circulation it is first necessary to make clear that the moving massecuite necessarily travels in a closed circuit, ascending past the heating surface and descending (for all pans of normal construction) in the central well. The hydraulic resistance, which is to be made a minimum for most effective operation, is the sum of the resistances experienced in the up-current and that experienced in the down-current. With the exception of the small

amount of water which is evaporated at the surface, the measure of the total up-current (in, say, gallons/sec) must be the same as the measure of the total down-current. If the free cross sectional area of the down-current (in the well) is, say, only one quarter of that of the up-current, then it necessarily follows that the velocity of movement in the down-current is four times that of the up-current. In order that the velocity of the down-current should be the same as that of the up-current it is necessary that the sectional area of the well should be the same as the free sectional area of the (outer) ascending zone. The ratio

$$\frac{\text{projected free area between the heating surface}}{\text{area of well}}$$

has been called by SMITH⁸ the circulation ratio and, as seen by the argument above, is a measure of the relative velocities in the well and in the up-stream. He claimed that this factor is vital to the final circulation rate attained in the pan as indeed it must as it affects the overall resistance to circulation.

Generally speaking however unit circulation ratios or conditions of equal velocity in the well and ascending zone should not be the aim of the pan designer for the reason that there are far more obstructions in the outer zone. The frictional resistance exerted by these obstructions is directly proportional to the average wetted perimeter with which the moving section of liquid is in contact. If we wish therefore to equalize the hydraulic resistances of the up- and down-streams – this indeed is the condition that the sum of the two resistances should be a minimum – we arrange that the ratio

$$\frac{\text{sectional area}}{\text{average wetted perimeter}}$$

should be the same in the up- and down-streams. The ratio above is equivalent to

$$\frac{\text{volume of zone}}{\text{total area of obstructions to that zone}}$$

in which the denominator includes the area of interaction between the up- and down-streams as well as the outer wall area.

For a pan of any given heating surface area consideration of the ratios above will permit a selection of the optimum well diameter. As a general rule most old pans in the sugar industry are underdesigned in this respect.

WADDELL⁹ who considers that a circulation ratio of 8 or 9 should compensate for the higher skin resistance of the heating coils, has concluded

that the centre wells of most pans are still far too small. He also has adduced evidence to show that there is often a large annular zone of interference between the up- and down-currents. This, he suggested, could be eliminated by the use of a thin walled baffle. He makes no mention, however, of how he would propose to adjust the wall for different heights of massecuite in the pan.

WADDELL⁹ also has comments to pass on the proper position of feed pipes. Fresh liquor fed into a pan is of lower density than the material already present and therefore feed can be used to augment natural convection if supplied immediately below the heating surface. WADDELL has suggested a perforated ring or star under the coils or calandria rather than a single pipe in the well. This latter indeed is a particularly poor arrangement as it tends to produce hydrostatic effects opposing natural circulation.

Ample circulation no matter how derived, produces a number of very desirable effects.

(α) It increases the heat transfer rate by augmenting natural convection with a system of forced convection.

(β) It reduces the temperature difference which might otherwise occur in the pan. This is effected by lifting bubble nuclei as soon as they are formed to regions in the pan where the hydrostatic pressure is lower and in which therefore boiling may take place.

(γ) Rapid circulation too gives a minimum risk of local undersaturations. Regions of incipient local low concentration or high temperature are rapidly mixed with other regions.

(δ) A reasonably rapid circulation rate is also essential for the purposes of keeping the sugar crystals in suspension. Being slightly denser than the saturated sugar solution crystals would tend to settle out in a true static mass and the settled crystals would simply tend to grow together as an agglomerate. The individually suspended crystals carried by the circulatory stream are given every opportunity to grow evenly in all directions.

4. The Effect of Temperature on Crystallization and Circulation

The overall temperature difference which provides the effective driving force for evaporation and circulation is equal to the difference between the temperature of the steam and the boiling point of the massecuite, or temperature of the pan. If, as is usually the case, exhaust steam at a constant pressure is used to provide the heat source the second factor, namely the temperature of the pan, controls the rate of evaporation. The temperature

of the pan may be adjusted by adjusting the pressure. Such a change could affect the rate of evaporation in two ways:

(1) A fall in pressure, or increase in vacuum, lowers the boiling point and thus leads to an increased temperature differential and so to an increased heat transfer rate.

(2) At the same time, however, the lower boiling point of itself produces an *increase* in the thermal resistance resulting in a lower heat transfer rate for a given temperature differential.

The cause of the lower heat transfer coefficient at low temperatures appears to be connected with the higher viscosity at those temperatures but there are other causes which are not well defined.

However, the net result of lowering the pressure on the massecuite is to produce some increase in the heat transfer rate but considerably less than that expected from the increased temperature differential. It is generally preferable, if an increased heat transfer rate is required, to work at the highest possible temperature but this may give rise to some destruction of reducing sugars. As a compromise, it has been claimed by DITMAR JANSSE¹⁰ that a boiling temperature in the range of 65°–70° C is preferable.

A relatively high boiling point has another advantage. It reduces the effect of the hydrostatic head on the boiling point. In a tall column of liquid the pressure on the surface is equal to the pressure in the vapor phase above the surface. The pressure at any point below the surface is necessarily greater than the pressure in the vapor phase. At a point distance z below the surface of the liquid each unit side has to support, in addition to the pressure of the vapor, a load of $\rho g z$ units of force per unit area, where ρ is the density of the liquid and g the acceleration due to gravity. If we denote by p the pressure at a depth z and p_0 the pressure in the vapor, then

$$p = p_0 + \rho g z$$

When p_0 is relatively low, *i.e.* when we are dealing with a reasonably low vacuum, the change in pressure with change in depth may be an appreciable fraction of, or even much greater than, the pressure p_0 . Roughly, 10" of sugar liquor increases the hydrostatic pressure by the equivalent of 1" mercury (absolute).

Now the boiling point of a liquid varies with the pressure. If a column of liquid is maintained strictly at a uniform temperature then, if the liquid is at the boiling point on the surface, it must necessarily be below the boiling points at all points below the surface. In other words, the boiling point of a column of liquid increases with the depth. Since there is a logarithmic

relation between boiling point and pressure the change in the boiling point with depth will be the more serious, the larger the change in $\log p$ with depth, *i.e.* the larger the change in $\log (p_0 + \rho g z)$ with z . This change will, of course, be greatest when p_0 takes its lowest value. In other words, the change in boiling point with depth is greatest at the highest vacuum. The boiling point of a saturated sugar solution for example increases by 1.2°C for each ft. increase in the depth at atmospheric pressure. At a 20" vacuum the increase in boiling point is 2°C per ft., at a 25" vacuum it is 5°C per ft. and at a 28" vacuum it is 11°C per ft.

Consequently if we are evaporating at a relatively high vacuum and material is raised to the boiling point at, say, 2 ft. below the surface that particular volume of material would be very seriously superheated if suddenly conveyed to the surface. Even in the case of a gradual transport to the surface a very considerable degree of flash evaporation must take place if the material is to maintain thermal equilibrium between the liquid and the vapor phases.

When a massecuite in a vacuum pan is circulating vigorously there is not much evidence that temperature differences as severe as those indicated above are experienced. HONIG¹¹, for example, claims that under good conditions the vertical temperature differences should not exceed 2°C . However, there is some evidence that the temperature in the well is appreciably lower than that immediately above the coils or calandria. Indeed it is this temperature difference which ultimately provides the driving force for circulatory motion.

5. Measurements of Pan Circulation

Various methods have from time to time been proposed for the measurement of the circulation occurring within a vacuum pan. The heat transmission recorder, it will be recalled from Chapter 8, gave a reading of a temperature difference which depends in principle on the rate at which the heated liquid mass is flowing past a body maintained at a temperature either higher or lower than the liquid itself.

A direct method of measuring circulation was first described by HONIG¹¹ and his associates and is generally referred to as the Java method. It uses two pairs of electrodes one vertically above the other. Each pair is connected to a bridge circuit for the measurement of electrolytic conductivity. From time to time the passage of bubbles or local irregularities in the massecuite causes a slight disturbance to the value of the electrolytic resistance between a pair of electrodes. By noting the difference in the time of arrival of a dis-

disturbance at the two pairs a direct measure of the time taken to travel a known distance was obtained. From this measurement, of course, could be calculated the velocity of movement of the irregularity which may or may not be quite the same thing as the velocity of the massecuite itself. There is some evidence for example that a bubble rising in a massecuite – particularly a large bubble, would travel faster than the massecuite itself. However, much less ambiguous readings may be obtained by introducing a lighter fluid (say water) to the pan and timing the arrival of the resultant disturbance to the conductivity at the two different electrodes. This Java method of measuring the rate of circulation has also been used by SMITH⁸ in his study on the relation between the rate of circulation and the circulation ratio and certain other factors connected with the design of pans.

An extension of the Java method has been described by DEDEK and HRUBY¹². They inserted five pairs of electrodes in different parts of the pan and took a series of consecutive readings obtaining thereby simultaneous measurements of the circulation rates at different points. They concluded that the most intensive circulation occurred at or near the surface and that the rate of movement decreased with increasing depth until in the deepest part of the pan the motion was so sluggish as to be incapable of keeping crystals in suspension. In some respects this finding is markedly at variance with that of the author and his associates and which will be treated in the following section.

WEBRE¹³ has given a method for estimating the average rate of circulation from the measured rate of evaporation assuming a state of equilibrium between the massecuite and the vapor phase at the top of the heating coils or calandria. This assumption may not, however, always be justified and WEBRE's method may be little better than an inspired guess.

The method which has been exploited by BOSWORTH *et al.*^{14, 15} involves the use of the principle of the hot-wire anemometer. This method measures the rate of heat loss from a standard hot surface at different points in the pan and correlates this heat transmission data with the speed of the flow of material over the heated wire. Since the essential metering instrument is small and portable it permits the measurement, almost simultaneously, of circulation rates at a whole number of different points within the pan and as such is a method for obtaining not only the circulation rate but also the whole pattern of circulation currents. As such the instrument will be treated in the following section. For the moment this particular section will be concluded with a discussion of other possible methods which have not necessarily yet been tried for the measurement of pan circulation.

A review of the methods available for the measurement of fluid flow has been given by BOSWORTH¹⁶. Not all the classes of instrument described could conceivably be modified for use in an enclosed space but some are worthy of attention. None, for example, of the classes of displacement, head, area, or head-area type of meter are suitable for modification for the purposes of measuring pan circulation. On the other hand, the class of impact meters, of which the cup anemometer and the pitot tube are typical examples could, at least in principle, be usable within an enclosed space. The severe erosion to be expected from the moving sharp angular crystals might, however, be a seriously limiting factor.

Among the thermal flowmeters are listed the hot-wire anemometer and the THOMAS meter. The former has already been adopted to the measurement of pan circulation. The latter is potentially useable and is perhaps worthy of a moment's attention.

The THOMAS flowmeter consists in a heat source placed symmetrically between two thermometers, one up-stream and one down-stream from the heat source. When the liquid is at rest the reading of the two thermometers will be equal because both will receive the same amount of heat from the source. When the liquid is moving, however, it will carry heat, by forced convection, preferentially to the down-stream thermometer which will then give a higher reading than the up-stream one. The faster the flow rate, the larger will be this temperature difference. The THOMAS meter thus measures both the speed and direction of the current and in this respect has distinct advantages over the hot-wire anemometer. Indeed by increasing the number of the thermometers to four, placed respectively at the four corners of a regular tetrahedron surrounding the hot body, it would be possible to get a complete measure of the magnitude and direction of flow in three-dimensional space. For work in an enclosed space the thermometers would be replaced by thermocouples or thermistors.

The last type of flowmeter mentioned is the chemical flowmeter where a contaminant is added at some point in the line and the time of picking up this contaminant at some point down-stream is noted. The Java method is essentially an application of the chemical flowmeter to the measurement of pan circulation.

6. Measurement of the Circulation Pattern

The flowmeters based on the principle of the hot-wire anemometer to which reference was made in the previous section, differ from the usual form of such instruments in that the temperature of the electrically heated wire or

surface is measured by a thermocouple for which one junction is welded to the hot surface and the other junction placed in the fluid a short distance away. The thermocouple then gives a measurement of the temperature difference between the hot body and its surroundings for any given electrical heat input. The more customary form of the hot-wire anemometer uses the resistance of the heating element itself to measure the temperature. The behavior of such an instrument would be quite unsteady if immersed in a fluid (such as a vacuum pan massecuite) which is subject to a fluctuating temperature and this was the primary reason for the adopting of the thermocouple type.

The first arrangement used has already been illustrated in Fig. 8/2 of Chapter 8 (p. 308). It consisted of a short length (about 1") of electrical resistance wire, of 23 S.W. gauge. To the centre of the wire was welded a fine thermocouple of 32 S.W. gauge for measuring the temperature difference between the wire and its surroundings. The heat input to the wire and thus the rate of heat loss to the surrounding massecuite was proportional to the square of the heating current I . If θ is the temperature rise produced by this current, the heat transfer coefficient is proportional to I^2/θ . This factor has been found both by measurement and in theory to be practically independent of the composition and purity of the syrup in which the wire is immersed, and to increase steadily when the velocity of flow over the wire is increased.

Before use the instrument was calibrated by immersing in a trough of flowing syrup and the variation of I^2/θ with change in the velocity of flow V was recorded. A large number of measurements showed that the change in I^2/θ was proportional to

$$v^{0.6}$$

and was independent of the direction in which the flow over the wire took place.

When calibrated, the instrument mounted on an electrically insulating plug was screwed into a long cold-drawn steel tube which was passed through a gland in the wall of the pan under investigation. By sliding the pipe through the gland the flowmeter could be used to measure the velocity of flow at any point on a traverse across the pan.

To take a series of readings under working conditions the current I was adjusted to give a reasonable value of θ (as measured by a galvanometer connected to the thermocouple). The instrument was then pushed across the pan and drawn back again, taking readings of θ at intervals depending on the degree of detail in the circulatory pattern required. The

results measured in the first instance as readings of θ and I were transformed to the form of I^2/θ and then compared with the calibration curve of the instrument.

Preliminary experience with a number of hot-wire elements of this nature showed that these instruments had ample sensitivity even when used with the type of robust galvanometer suitable on a factory floor. However, the instruments showed two faults which were at least a source of annoyance to the operators. In continued factory use the hot wire junction tended to catch fibres which built up a tight knot around the heated surface and tended to change its calibration. It proved indeed necessary to remove the instrument from the pan at least once a day and to clean the hot wire.

In addition the instrument was unnecessarily quick acting. A few weeks experience rapidly showed that the whole pattern of circulation in a vacuum pan is subject to a continual state of flux. These fluctuations are particularly intense in certain pans and no sensible sort of reading of the velocity is possible unless there is some smoothing of the more rapid fluctuations. To meet this situation an indirectly heated hot-surface instrument was devised. The first type is also illustrated in Fig. 8/2 of Chapter 8 (p. 308).

In the indirectly heated instrument an electrical heating coil heats an insulated metal capsule. The capsule is of thin walled monel metal some 2" long by 3/8" diameter. Monel metal has a high thermal e.m.f. relative to copper so that the hot junction could be made by welding internally a copper lead to the head of the capsule. This copper lead was electrically insulated from the heater. The cold junction was constructed by brazing a monel metal - copper thermocouple to the lower part of the capsule, the monel arm being connected to the capsule and the copper arm to a copper lead.

In this instrument the internal hot junction cannot catch any fibres; the cold junction may do so but this does not affect the calibration. Again the large monel sheath and its insulated internal heater has a relatively high thermal capacity. The instrument therefore satisfactorily smooths out the effect of rapidly fluctuating circulation. The sensitivity under operating conditions similar to those of the hot-wire instrument is a little less than that of the latter but is still ample for practical purposes.

The hot capsule instrument described above has been mounted on a long steel tube and used in the same way as the hot wire instrument to explore the circulation pattern in a number of vacuum pans in a series of factories. The instrument exhibited one failing associated with its high thermal capacity. It took a comparatively long time, sometimes up to five minutes, to settle down to equilibrium after movement into a new position.

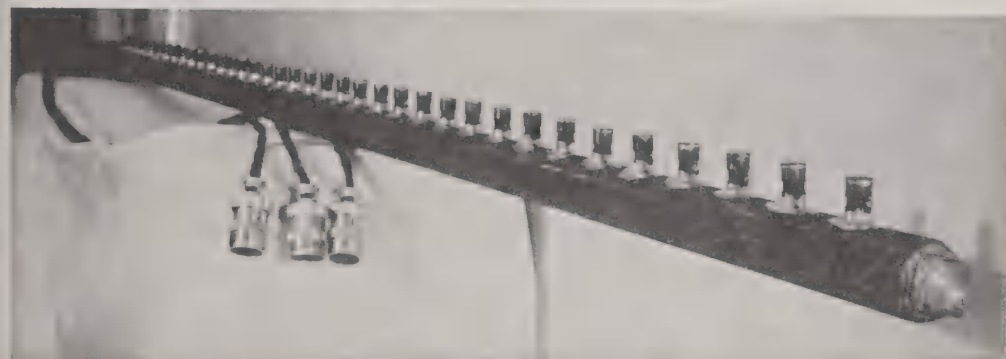


Fig. 10/1. An array of 36 flowmeters.



Fig. 10/2. Cathode ray oscillograph.

It therefore took quite a long time to get adequate readings to give the fine detail of the circulation pattern in a traverse across a pan. Indeed there

was evidence in several instances that the overall flow pattern had changed quite considerably while the readings were taken.

It appeared that there is only one real way of eliminating this difficulty, that is to mount a number of similar instruments in semipermanent positions so that these may come to thermal equilibrium with their surroundings. Then simple electrical switching will give a rapid successive series of readings at the different fixed points.

For purposes of mounting a multiple array of hot surface instruments on a common structure the capsule type was modified and made smaller. A diagram of the components and of the completed instrument has already been given in Fig. 8/3 of Chapter 8 (p. 309).

An array of 36 flowmeters of this type having thermal characteristics identical to within 5% are shown in Fig. 10/1 mounted at regular intervals along an 8'6" length of 2" seamless steel tubing. The wiring to the heaters and thermocouples of each instrument is carried through the pipe and leads to the multi point junction boxes shown. The response from the thermocouples was passed through a chopper-amplifier and used to actuate a cathode ray oscillograph which, in effect, could be caused to draw, for every rotation of the selector switch, a trace of the circulation pattern across the traverse made by the pipe. A representation of the cathode ray circuit and its ancillary equipment is given in Fig. 10/2.

7. Circulation Patterns and their Interpretation

The simplest form of circulation pattern obtained is illustrated in Fig. 10/3. This pattern was obtained from a coil pan boiling *C* massecoites and filled

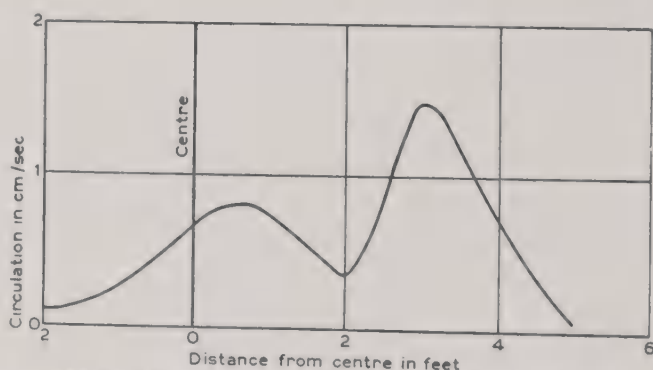


Fig. 10/3. Meter at 1500 gallons, massecoite filled to 1900 gallons, conductivity 74.

to the 1900 gallon mark while the flowmeter was inserted at the 1500 gallon mark. The pattern consisted of two waves only, one reaching a peak

about 2 ft. from the wall and the other about 9" from the centre of the well. Since the instrument is not sensitive to direction the two peaks probably correspond to the up- and down-streams respectively.

When the same pan was examined at a later stage in the boiling operation, the rate of circulation had shown a considerable decrease, the pattern had

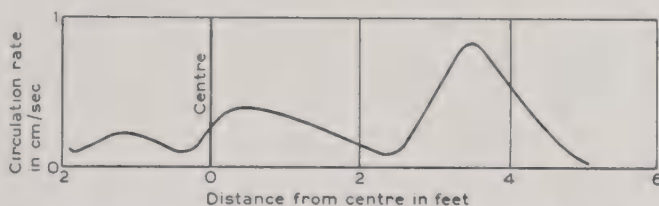


Fig. 10/4. Meter at 1500 gallons, massecuite filled to 3200 gallons, conductivity 61-68.

become sharper, pointing to more clearly defined zones of movement, and there was some tendency for the central stream to divide into two (see Fig. 10/4), a tendency which was much more marked in surveys taken in other pans and at deeper depths. This tendency to bifurcate can only mean that the down-stream in the well is tending to spread out and rejoin the up-current while still quite an appreciable distance from the bottom of the pan.

Fig. 10/5 represents the pattern obtained in the same pan and with the same massecuite, but examined at a higher (the 2800 gallon mark) level. Here movement in the centre is more pronounced and movement near the

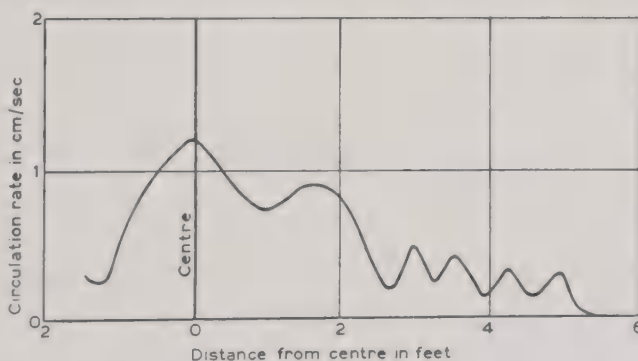


Fig. 10/5. Meter at 2800 gallons, massecuite filled to 3200 gallons, conductivity 69-76.

edges of the pan consists in a series of maxima, probably the individual up-currents arising from the different turns of the heating coil.

This pattern of 'shadows of the coils' was always more pronounced in pans boiling higher grade material. Fig. 10/6 is the record of a mill pan boiling *B*-massecuites. Fig. 10/7 of one boiling mill *A*-massecuites and Fig. 10/8 two patterns of a pan boiling refinery massecuites. The two

patterns shown in Fig. 10/8 were obtained respectively 10 and 180 minutes after starting up the skip and illustrate the overall decrease in the circulation rate as the material becomes stiffer. Comparison of the magnitude of the circulation rates for the different grade of material may also be obtained by comparing the ordinates of Figs. 10/5, 10/6, 10/7 and 10/8.

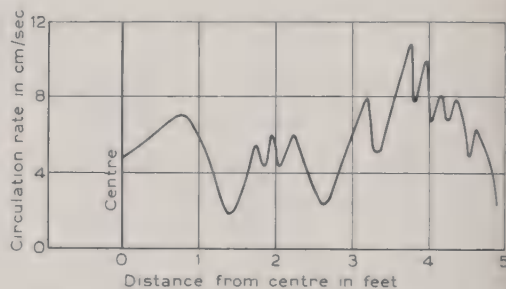
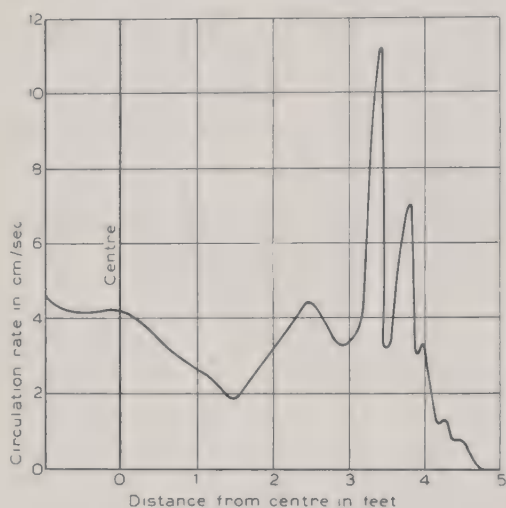


Fig. 10/6. Meter at 2500 gallons, massecuite filled to 2700 gallons, conductivity 75.
Fig. 10/7. Meter at 2300 gallons, massecuite filled to 2500–2800 gallons, conductivity 73–74.

Examples of flow patterns in which the general circulation appears to miss the central core are given in Figs. 10/9 and 10/10. Both refer to mill *B*-massecuites. In either instance the average overall circulation rate appears to be quite good but in Fig. 10/9 the down-stream has apparently completely split into two at the level at which the flowmeter was inserted.

Fig. 10/10 shows a still more extreme case. In this instance the flowmeter had been inserted at 1000 gallon mark in a pan boiling 3600 gallons. One notable peak only – indeed quite a pronounced one – was found some 3 ft. from the wall. A reasonable interpretation of this diagram was that the flowmeter had passed through the heel of the system of convection currents and that the massecuite at the recorded peak was moving neither upwards or downward but over more or less horizontally from the well to the outer rising stream. Fig. 10/11 consists of data obtained at the same time as that of Fig. 10/10 but at a higher level (namely the 2000 gallon mark). In this instance the flow pattern seems reasonably normal although perhaps the well current is rather weak. The pan which gave the flow patterns represented by these two figures has long been regarded by the operating mill staff as a poor circulator. The diagram makes the reason plain. The rate of

movement in the active part of the pan is not abnormally slow but there is apparently a considerable portion of the pan volume, particularly that at the bottom of the well which is outside the reach of the convection stream.

The circulation pattern given by a calandria pan usually shows far less

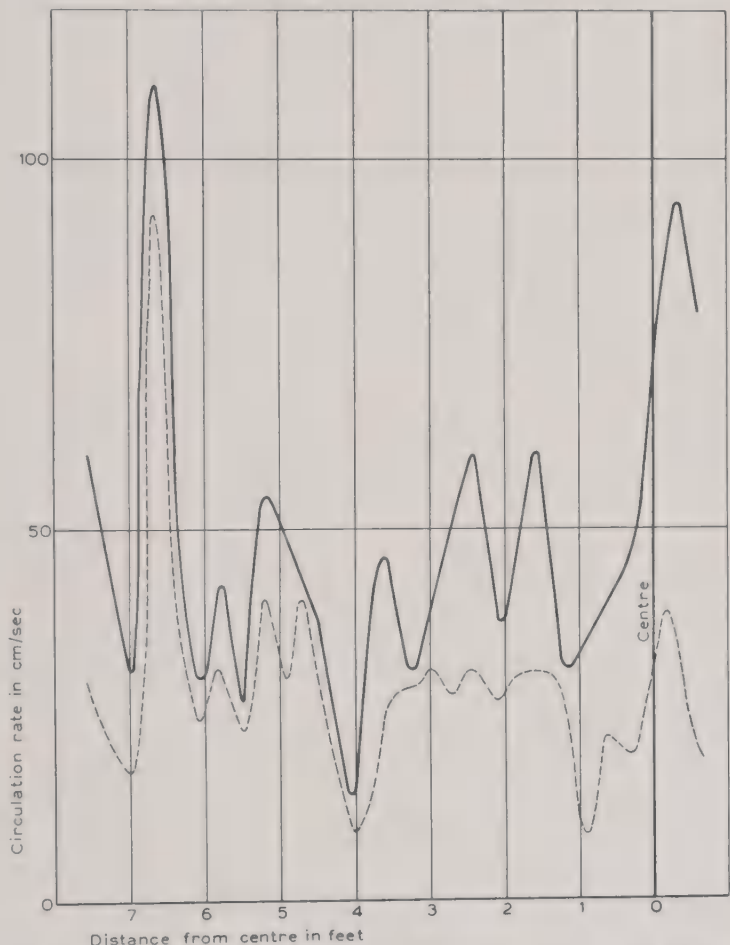


Fig. 10/8. Refinery massecuite. Fixed set of flowmeters inserted through the coils.
 — = 10 minutes after start-up; - - - - = 180 minutes after start-up.

detail than that of the coil pan. There is no notable change in the rate of movement in the different points on the traverse across the pan and no sharp line of demarkation between the well and the upcurrent. The two curves in Fig. 10/12 represent the results of a traverse made just across the top of the calandria, the upper curve was obtained when the massecuite was relatively light and the lower curve when it was heavy and the pan was full.

As a result of a program of investigation with the hot surface type of flowmeter the following conclusions were obtained:

(1) The mean circulation rates for the different grades of mill massecuite are roughly

A-massecuites 10 cm/sec
AB-massecuites 8 cm/sec
B-massecuites 4 cm/sec
C-massecuites 2 cm/sec

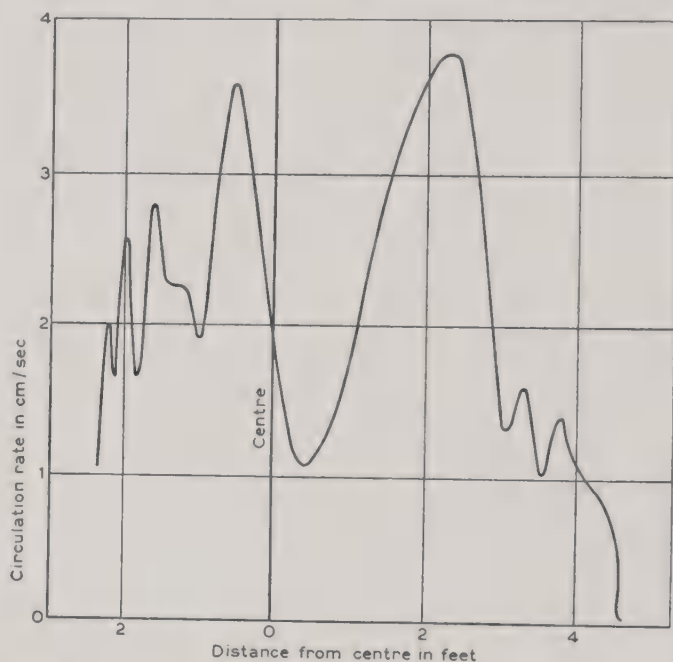


Fig. 10/9. Meter at 1400 gallons, massecuite filled to 2400 gallons, conductivity 72-76.

For refinery shipment massecuites a comparable figure is 20 cm/sec.

Different pans do not show very great departures from these average figures, although certain points may show excessively high local rates of flow, up to 5 or 10 times the average rate.

(2) There has been found no consistent evidence that pans suspected as

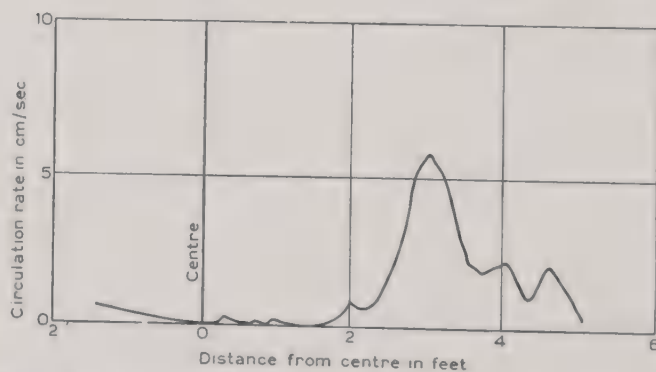


Fig. 10/10. Meter at 1000 gallons, massecuite filled to 3600 gallons.

being poor circulators from their mill performances show low average rates of flow. Indeed in some instances pans suspected of being poor circulators showed an average circulation rate which was high for the class of masse-cuite boiled.

(3) Suspected poor circulating pans do, however, show abnormalities

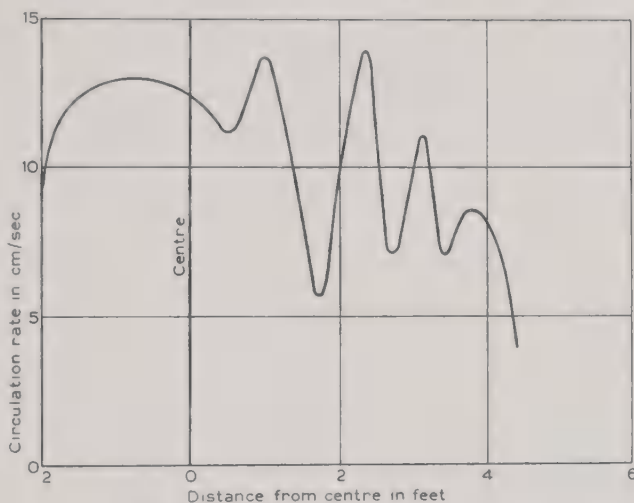


Fig. 10/11. Meter at 2000 gallons, masse-cuite filled to 2000–5000 gallons.

which may indicate the origin of their inferior performances. In many instances such pans gave very different circulation patterns at the different levels, the rate usually being much less at the lower, and abnormally high in

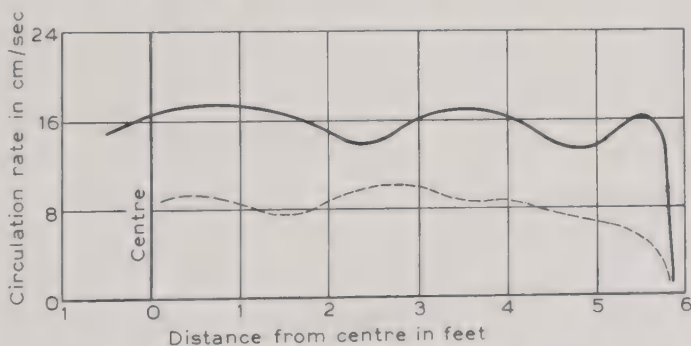


Fig. 10/12. Meter at 2700 gallons. — = masse-cuite filled to 3200 gallons; - - - - = masse-cuite filled to 6000 gallons.

the upper levels. Such a state of affairs could be taken to indicate that the apparent high circulation is due to a swirling motion in the upper part of the pan. In many instances too it was noted that the down-stream divided between the 2000 and 1000 gallon mark. Such behavior of the circulation pattern strongly suggests the presence of a stagnant pocket at the bottom

of the well. In other instances too the outer flow pattern tended to pull away from the wall in the lower part of the pan. This again would indicate dead pockets near the walls in the localities indicated.

The pattern for a pan with a particularly good performance, on the other hand, tends to maintain the same shape right through the different depths.

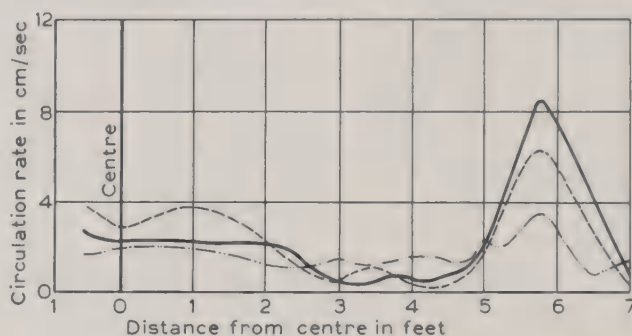


Fig. 10/13. — = Meter at 2100 gallons (curve C); - - - - = meter at 3600 gallons (curve B); - · - · - · = meter at 6400 gallons (curve A). Massecuite at 7000 gallons, conductivity 72.

The three curves shown in Fig. 10/13 refer to such a pan. This particular pan was boiling a mill *C*-massecuite when examined and circulation patterns were obtained at the 6400 gallon level (curve A), the 3600 gallon level (curve B) and the 2100 gallon level (curve C). Each curve reproduces the main features of the one below and there is no crowding together of the up and down streams in the lower part of the vessel.

(4) The plot of the circulation rate versus the distance from the centre on a given traverse may show a number of peaks. There is usually a maximum at or near the centre due to the down-stream in the central well. If the central well is small and cramped, this maximum may be fairly sharp. A little further out from the centre there is usually a zone of interacting currents where the mean measured circulation rate is low. Further out again the up-stream is encountered. This up-stream may consist of one or more maxima, the pattern being frequently particularly complicated when the measurements are taken above the level of the heating coils. This pattern has been attributed to the influence of the individual coils of the heating surface. Calandria heating surfaces do not give this pattern of repeating maxima.

(5) In all instances rates of circulation tend, as might have been expected, to decrease as the pans are heavied up. In some instances the decrease is particularly rapid and this may indicate that a suitably situated and designed flowmeter could be a valuable ancillary tool to the sugar boiler. The study of the placement of such instruments for satisfactory performance is a matter

requiring very careful consideration. In many instances the process of heavy-ing-up was accompanied not only by a decrease in the overall circulation rate, but also with a change in the shape of the circulation curve, often with a movement of the position of maxima away from the walls and the central core of the well. Placement of the measuring instruments in such a position that the circulation pattern draws away from them at any particular stage in the boiling would mean that the reading of that instrument would become useless for control purpose at that stage.

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CHAPTER 11

NATURAL AND MECHANICAL CIRCULATION IN VACUUM PANS WITH PERFORMANCE DATA AND TESTS

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1. Circulation in Vacuum Pans

(a) *Introduction*

In sugar vacuum pans satisfactory circulation is the indispensable requirement. It is brought about by the formation of vapor bubbles at the heating surface, which lighten the massecuite and make it rise. Designers take care so to arrange this heating surface as to leave a considerable open space in the centre for the passage of the liquid to the bottom for a new circuit after having liberated the vapors at the boiling level.

The faster the rate of evaporation, the better the circulation; and without evaporation there would be little or no circulation. To facilitate the movement it is very important to provide smooth and easy passages with a minimum of impediments and obstructions, because the force available for producing motion of the heavy viscous massecuite is limited, and decreases as the level rises and the rate of evaporation dwindles down at the end of the operation.

(b) *Downtakes and Tubes of Calandria Pans*

Along these lines calandria pans as now built have downtakes sometimes as large as one-half the pan diameter, where a few years ago they were only one-fourth. Some pans even have deflectors to project the rising flow of massecuite away from the centre towards the shell, with the idea of preventing the mixing of the hotter stream in the outer periphery with the cooler material returning from the boiling surface, as this might interfere with the normal up and down currents.

The old established standard of tubes 4" (101.6 mm) diam. has been

reviewed to determine if anything is to be gained by using other proportions. 5-Inch (127 mm) tubes have been tried, and whereas their use decreases friction and provides freer circulation, the loss of heating surface is very considerable to the point of becoming prohibitive. At the other extreme, 3" (76.3 mm) tubes have been generally adopted in Puerto Rico

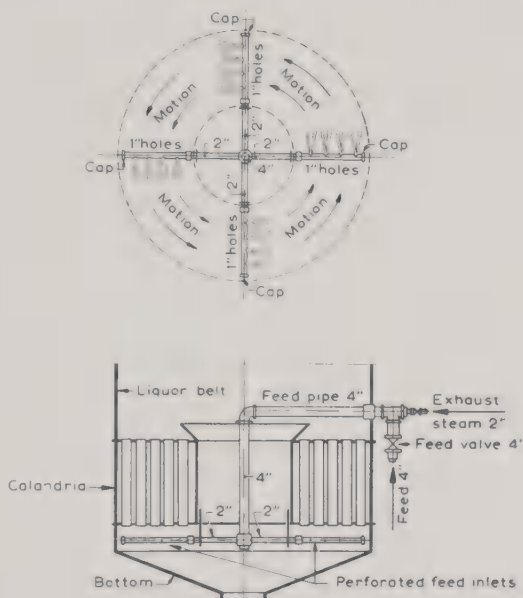


Fig. 11/1. Suggested method of feeding vacuum pans with CLAASSEN system of steam injection.

with fair success. One big advantage is that it is possible to install the same amount of heating surface in a calandria 3 ft. (0.915 m) high as in one 4 ft. (1.220 m) high with 4" (101.6 mm) tubes, and this makes a much smaller footing for the strikes. On the other hand, with low purity massecuites of high viscosity poor results are obtained when the level exceeds 4 ft. (1.220 m) above the tube sheet. This difficulty can be overcome by the proper distribution of feed below the heating surface, accompanied by the use of the CLAASSEN system of feeding low pressure steam with the syrup or molasses into the pan (Fig. 11/1). This difficulty does not occur with high purity strikes, and does not exist where mechanical circulation is installed.

Regarding the length of the tubes, there is no doubt that per sq.ft. (0.0928 sq.m) short tubes will give greater heat transmission. Some hold the opinion that it does not pay to use tubes longer than 36" (0.913 m), in spite of the reduced heating surface. Tests have been made on a pan so equipped in a sugar refinery, and the evidence obtained points to the correctness of this premise. Certain it is that there would be less danger of

heat injury, and that the volumetric proportions would be more favorable, not to mention the saving of copper tubes.

(c) *Coil Pans*

In a number of sugar producing countries the old familiar coil pan is becoming obsolescent, very few being built compared to the number of new calandria pans installed. The principal objection is that they are more selective and peculiar as to the quality of steam or vapor to be used. In the ordinary sugar factory it is not possible to effect steam economies so necessary for fuel saving unless exhaust steam or juice vapors can be used to the fullest extent for pan operation. Another objection is the longer time required for their operation compared with the fast work of present day calandria pans. Upkeep and repairs required are higher, especially if 'tight' boiling is carried on.

It was formerly thought that calandria pans could never produce sugar of as good quality as coil pans. This assumption has been completely overruled by the collected practical experience, as it is now possible not only to produce sugar of excellent quality with vacuum pans of the calandria type, but the heat injury to the products is reduced due to lower steam temperatures.

Nevertheless, there have been significant improvements in coil pan design, the most important of which is the use of tubes of elliptical cross section with their long axis in a vertical position (Fig. 11/2). This gives a greater area between the tubes for free circulation, and good performances have been recorded. This design has found many applications in Australia. This revision of the old type pan has enabled them to operate on exhaust steam by installing more heating surface.

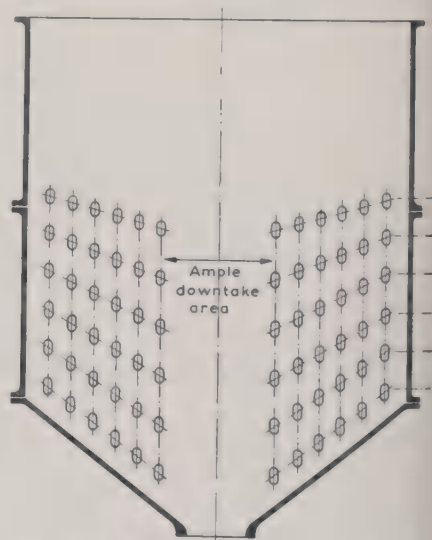


Fig. 11/2. Australian coil vacuum pan with tubing of elliptical section, producing fast circulation.

(d) *Ring Type Calandrias*

The GRÄNTZDÖRFFER heating element (Fig. 11/3), known in America as the 'Ring Type Calandria', undoubtedly offers a minimum of resistance to the passage of massecuite through it, and thus constitutes a very notable achieve-

ment. As indicated by the sketch, it is made up of a succession of vertical annular rings into which steam is fed. The upper parts of these rings are all at the same level, but below they extend down to conform more or less with the shape of the bottom, so that the rings are not all of the same height to avoid leaving a quantity of massecuite idle below them. There are in

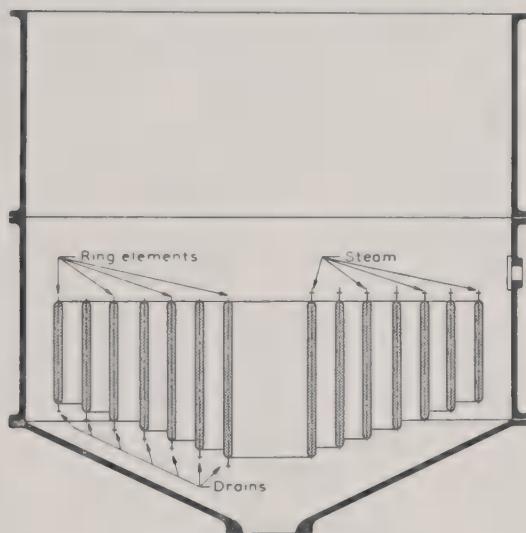


Fig. 11/3. Vacuum pan with GRÄNTZDÖRFFER type heating surface, made of concentric vertical rings, having minimum possible friction.

reality two downtakes, one in the centre and an annular space between the outermost ring and the body of the pan. Generally speaking, the operation is with reduced pressure live steam, but by increasing the number of ring elements operation can be with exhaust steam. This, however, impairs the best feature of the design, which is the remarkably free open space between the heating elements for the unobstructed passage of circulation with minimum friction.

This design has found extensive applications in the British sugar refineries, where by its use it has become possible to operate the system of heavy boiling, completing the white sugar crystallization in three skips instead of the conventional four as a result of the greater pan yields, which attain as high as 65% against the current practice of around 50% or even less on syrup skips. The fillmass is dropped at about 95 brix, where the fluidity becomes so reduced that the pan cannot be discharged without ample flushing with syrup from a previous skip of the same purity. Upon reaching the mixer, which is of very rugged construction, the brix is reduced to 9-90, at which it is suitable for use in automatic centrifugals.

It might be mentioned in passing that this pan does not produce sugar

crystals free of conglomerates, as has been accomplished by good calandria pans with mechanical circulation and the new controls described later in this chapter.

(e) *The Shape of the Bottom*

Usually the bottom of pans is made conical for the unimpaired discharge of the massecuite, being careful to leave enough clearance at the edge to permit the rolling of tubes. Since the first pans were all of the coil type, the deep cone has been inherited, and, with calandria pans, the objection of having a considerable volume of stagnant material is a problem. It has been found that for proper discharge the angle of the bottom need not exceed 20 degrees with the horizontal. The saucer type bottom, very shallow, was introduced as an improvement, and it is even streamlined with a conical projection upwards. This has imposed the necessity of having the discharge valve off centre at the lowest point otherwise some massecuite would remain. Even now massecuite does remain, and that is the big objection. It is easily possible to go too far in reducing the capacity of the bottom, as this involves area restrictions which impair free passage of the massecuite from the downtake to the tubes. In some cases it has been necessary to install a ring between these shallow bottoms and the calandrias to overcome this trouble (Fig. 11/4).

(f) *The Steam Side of the Heating Surface*

Since circulation is produced by the formation of vapor bubbles at the heating surface, attention must be given to the supply and distribution of steam and the removal of the condensation and non-condensable gases to obtain maximum and uniform heat transmission throughout, free of local inadequacies.

Many patterns of steam distribution have been used in calandria pans, and the results have not always been satisfactory.

One very simple way (Fig. 11/5) is to have an annular space around the calandria; omitting all baffles, entering ports and grids, admitting steam

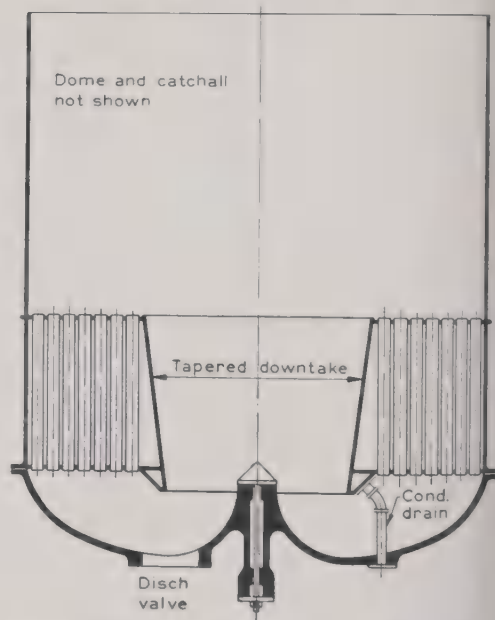


Fig. 11/4. Hawaiian vacuum pan with shallow bottom.

at two points tangentially. This offers a minimum of friction and a perfectly uniform supply of heat to all parts around the periphery. The condensation and gases have to be taken out from the centre, close to the downtake. There are no steam lanes in this system, and the tubes take up the entire area between the shell and the downtake, except where some have been omitted near the centre for condensate drains and gas vents.

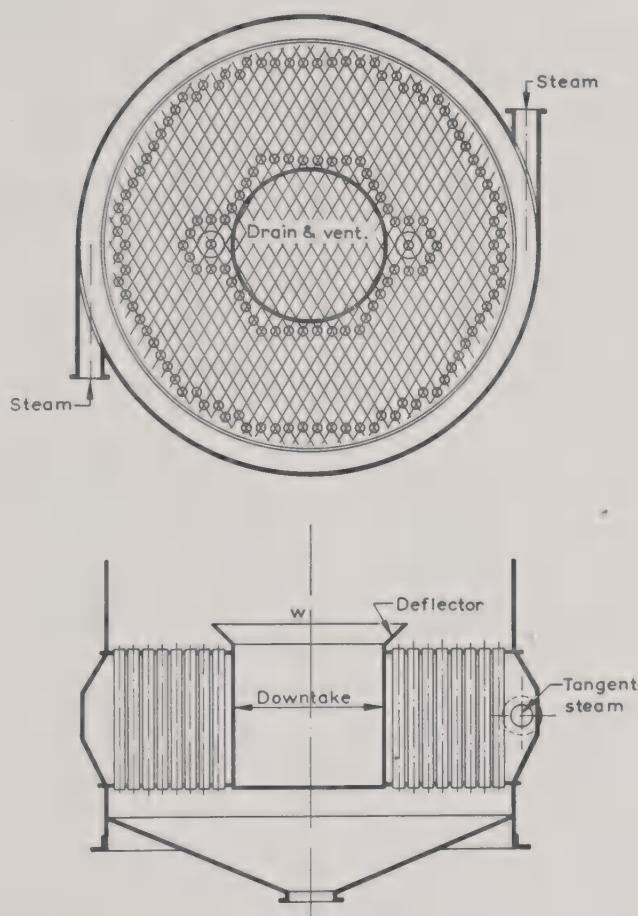


Fig. 11/5. Calandria vacuum pan with annular steam space and twin tangential admission.

The above design involves the cost of providing the annular space and has the disadvantage of having both the condensate drains and vent pipes inside the pan, where they are subject to severe strains during operation, and hence involve considerable upkeep.

Some late designs avoid the use of the annular space, making the shell of the calandria cylindrical (Fig. 11/6). To obtain proper distribution of steam, a number of tubes are omitted in front of the one steam inlet, leaving a wedge-shaped open space which is enclosed with plate extending from

the upper to the lower tube sheet. This enclosure is provided with uniformly distributed perforations whose total area is about equal to that of the steam inlet. Thus, the flow of steam is directed as wanted, preventing haphazard movement which might by-pass some of the tubes. The condensate is removed from the shell of the calandria on the outside through a

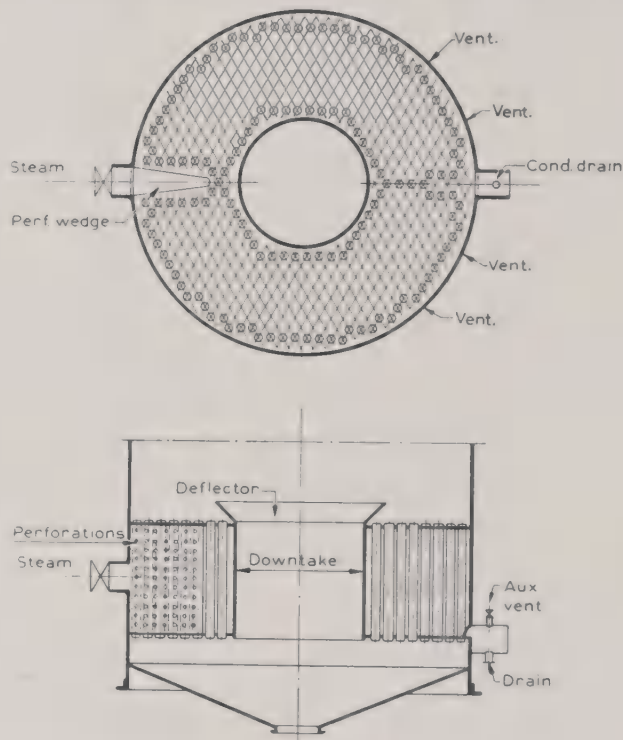


Fig. 11/6. New system of steam distribution, drainage of condensate and quadruple vents for calandria pans.

proper outlet of ample area. The venting also is done from the outside by the use of four small connections on the shell slightly above the lower tube sheet and equally distributed radially so as to occupy perhaps 90 degrees of the periphery, this segment being directly opposite the steam inlet.

When the pans are heated with juice vapors in the beet sugar industry, there will accumulate immediately below the upper tube sheet a layer of ammonia gas liberated from the beet juices being evaporated, and supplemental vents must be provided at that point; otherwise, not only will the heat transmission be impaired, but the inside upper ends of the tubes will be attacked if they are made of copper.

There are many other designs whose details are not given here. The appraisal of their value must be made on the basic principles outlined above. In some cases baffles or guides between the tubes have been provided for

driving the non-condensables to one point for removal. Theoretically this offers advantages, but it has not worked out very well in practice, certainly not so well as the two designs above.

(g) *Floating Calandrias*

Many pans have been built with floating calandrias (Fig. 11/7) which consist of a cylindrical drum with tubes, suspended inside the pan near the bottom,

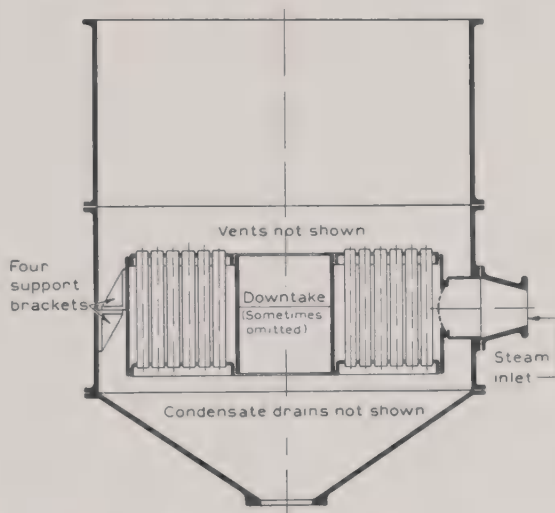


Fig. 11/7. Current type of floating calandria vacuum pan now obsolete.

with drains and vents. Here, circulation is up the tubes, radially towards the shell and down the annular space between the floating calandria and the body of the pan. A central downtake is also provided, of small diameter. This has developed to be a very inefficient design, which has given poor results in crystallization of sugar, with the production of false grains and conglomerates. Some of these pans have two calandrias, superposed, and some even have inclined tube sheets, which necessitates the installation of tubes at right angle to the conical tube sheet, or the objectionable alternative of keeping the tubes vertical and rolling them at an angle. It is our opinion that this system has little to offer over the less expensive and simpler standard design.

(h) *Supplemental Vents*

In view of the fact that most non-condensable gases (air and CO_2) are heavier than steam, and hence accumulate just above the layer of condensate on the lower tube sheet, it has often been possible to achieve consid-

erable improvements in performance by installing a gas-separating chamber in the condensate drains just after leaving the calandrias, with gas vents in their upper part discharging to the atmosphere. Apparently much of this gas is drawn into the drain pipes by the flow of condensate. This device not only clears the pipes, but removes a considerable quantity of gas which would otherwise remain in the calandria.

(i) *How Fast is Natural Circulation?*

In Australia they have developed equipment by the use of which it has been possible to measure the velocity of circulation in massecuite boiling in a pan. The results of these investigations have been reported in the *Proceedings of the Intern. Soc. of Sugar Cane Technologists*. The objection is the complication involved and the elaborate preparations needed to be able to make the observations.

From our standpoint, the most important matter is not how fast the massecuite is moving, but how slowly. This occurs in the tubes or at the heating surface while heating and before boiling, and this phase exists during all strikes at all times, because when the massecuite comes in contact with the tubes in their submerged position the temperature is always below the boiling point. A simple way to make an estimate of the speed of circulation during the heating phase is the following.

First, the rate of evaporation or steam consumption must be known at regular intervals during the strike. Then, the pan must be equipped with two simple angle thermometers mounted one just below the calandria to get the temperature before entering the tubes, and another slightly above giving the temperature upon leaving them.

It is assumed that these two thermometers give the rise in temperature. The number of tubes, their diameter and length are known, and hence the amount of evaporation in each tube. The heat is absorbed by the massecuite by the difference of temperature between the two thermometers. The weight per cubic foot is known from the brix, and the specific heat of the massecuite is also known. With these data it is not difficult to estimate with

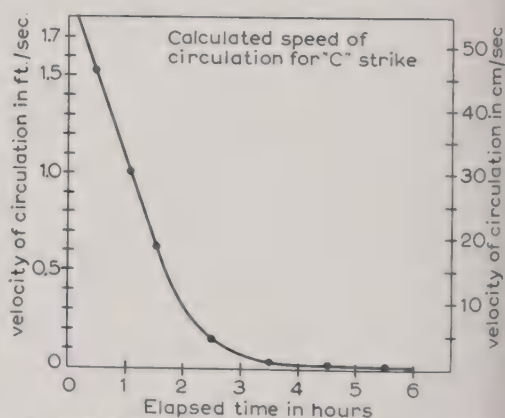


Fig. 11/8. Estimated speed of natural circulation in tubes of calandria pans during the heating phase.

fair accuracy the velocity in the tubes. A test made in Cuba on a well designed calandria pan gave the following results for a *C*-strike: (Fig. 11/8).

First hour	1.52 ft./sec	= 465.00 mm/sec
Second hour	0.62 ft./sec	= 189.40 mm/sec
Third hour	0.15 ft./sec	= 46.00 mm/sec
Fourth hour	0.03 ft./sec	= 9.17 mm/sec
Fifth hour	0.015 ft./sec	= 4.59 mm/sec
Sixth hour	0.010 ft./sec	= 3.05 mm/sec

At the beginning of the strike there is violent evaporation in the tubes, and this has a pumping effect and increases the velocity; but towards the end, when evaporation has dropped to almost nothing, there results stagnation, and not circulation.

(j) *Temperature Conditions in Vacuum Pans*

The matter of temperatures in vacuum pans must have careful consideration to see what influence this may have on performance, not only on the speed of operation, but also the possible damage which may accrue from conditions shown to exist.

The point was made earlier that for circulation to take place without mechanical means, it is indispensable that evaporation takes place at the heating surface. This heating surface is always submerged, and the amount of submergence increases as the level of the massecuite progresses to its ultimate height of 6 or 7 ft. (1.830 to 2.130 m) above the calandria. This means that temperatures in the tubes must correspond to the reduced vacuum resulting from the weight of the superposed massecuite.

To make this point clear, a graph (Fig. 11/9) has been prepared in which it is assumed that a *C*-strike is being made with material of 60 apparent purity, and that supersaturation* is carried at 1.325, which corresponds more or less to normal work. There are tables by the writer giving the boiling point rise of massecuite at various purities and temperatures at saturation, and at supersaturations of 1.25 and 1.40 representing the working limits of the operating zone. If supersaturation is allowed to reach 1.48, spontaneous nucleation occurs. Not to complicate the situation excessively, it is

* Supersaturation, as understood in this text, is the ratio of the amount of solids dissolved in the liquid per 100 parts of water to the amount of solids per 100 parts of water at saturation at a given purity and temperature, and is determined according to the data given by EUGENE C. GILLET in his book *Low Grade Sugar Crystallization*, page 15, on the basis of the boiling point rise.

assumed that the selected supersaturation of 1.325 will be invariably maintained.

Before arriving at this temperature graph preliminary information must be prepared.

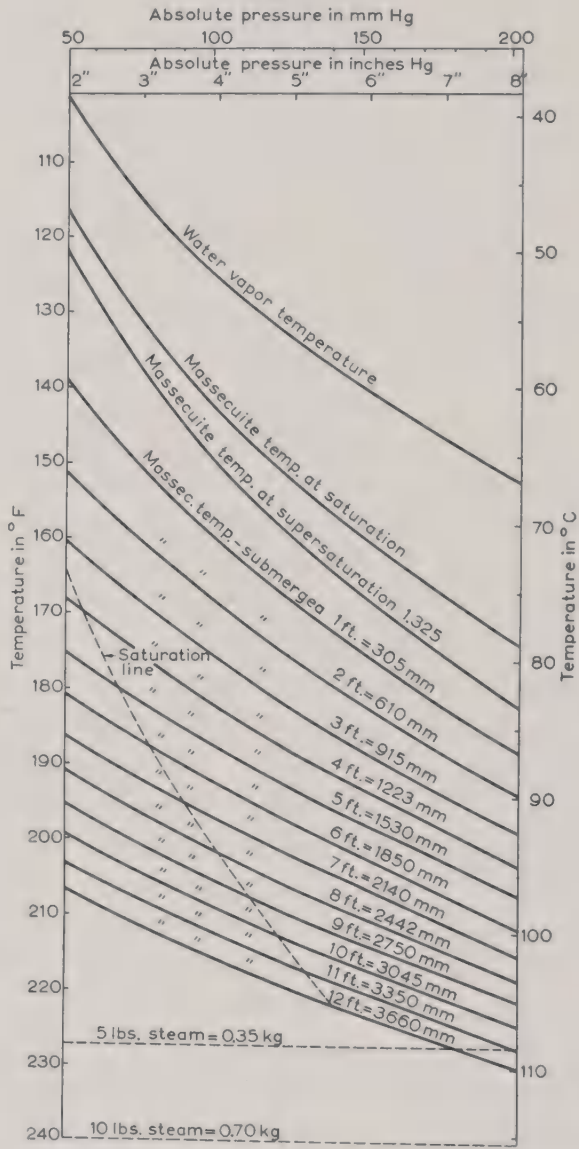


Fig. 11/9. Temperature-pressure chart for 60 purity massecuite boiling in vacuum pans.

(k) Boiling Point Rise for 60 Purity

From the operating data sheets for vacuum pan control instruments by the writer, the accompanying chart (Fig. 11/10) was plotted for an apparent purity of 60. The ordinates represent the boiling point rise from 15–32° F

on the left hand side and from 8–18° C on the right. The abscissae give massecuite temperatures from 120–240° F at the bottom and from 49–113° C at the top.

The lower straight line curve shows the b.p.rise at a saturation of 1.00. Then come two others for supersaturations of 1.25 and 1.40 enclosing

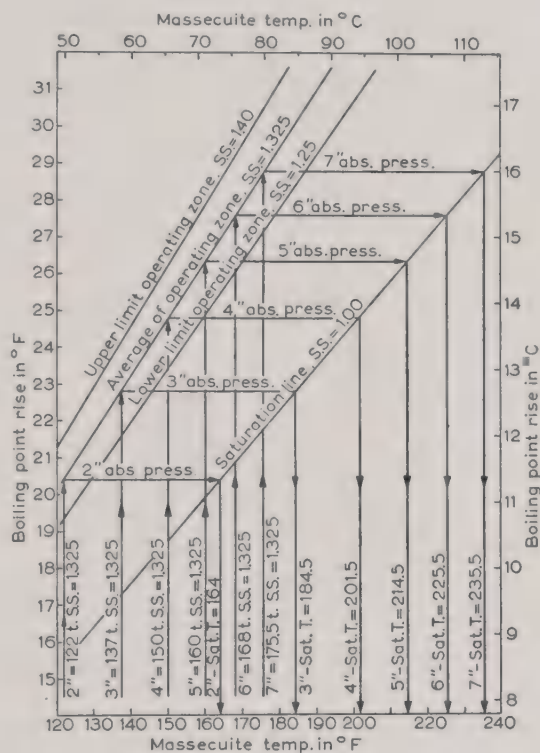


Fig. 11/10. Boiling point rise chart for 60 purity.

the working zone. The line between these two represents the average at 1.325. With this chart, it is possible to read off the b.p.rise at any boiling temperature within the range. If any point on the 1.325 curve is taken and a line drawn horizontally to the right until it intersects the saturation line, by dropping from this point to the base line below, there is obtained the temperature to which massecuite at a supersaturation of 1.325 must be heated to revert to saturation. This feature will be used to determine the saturation points at various vacua, which will be plotted on the graph.

(1) *Hydrostatic Head Loss*

The second preliminary chart (Fig. 11/11) was prepared to show the increase in the boiling temperature of massecuite as the submergence increases

from zero at the boiling level to the maximum depth probable in running a normal strike, taken at 12 ft. (3.650 m). Abscissae represent submergence in ft. at the lower scale and in mm at the upper one. The ordinates give the increase in boiling point rise in $^{\circ}\text{F}$ on the left and in $^{\circ}\text{C}$ on the right. Curves have been plotted for absolute pressures from 2" to 8" inclusive with metric equivalents, all based on a brix of 90, representing a specific gravity of 1.48. At this density each foot of massecuite involves a loss of vacuum of 1.29 inches of mercury (32.8 mm.) It is true that towards the end of operation, when the final concentration is given, the brix, and hence the specific gravity would also increase. This is of relatively short duration, and so, for avoidance of complications, the correction is omitted.

(m) Boiling Temperature Graph

The main boiling temperature graph (Fig. 11/9) was prepared for an apparent purity of 60. It is the purity of the mother liquor that determines the

b.p.rise, hence there will be a material deviation from our figures, because as sucrose is crystallized from the mother liquor, its purity will gradually decrease until, at the end of the operation, it will be around 40–42. This means that the conditions revealed by this study are materially better than actuality. In many tests of C-strikes, the b.p. rises at the ends reach as high as 36°F (20°C), where the estimated maximum at the surface is only 24°F (13.3°C). So the deviation at the end might reach 12°F higher (6.66°C). It would be uncertain to make an allowance for this in view of the undetermined fluctuations, so we will proceed on the basis of an unaltered purity of 60.

Ordinates represent temperatures $^{\circ}\text{F}$ on the left and temperatures $^{\circ}\text{C}$ on the right. As abscissae there are two scales on top, one giving absolute pressures in inches of mercury, and the other absolute pressures in millimeters of mercury. The uppermost curve gives saturation vapor temperatures obtained from steam tables. The second curve below gives the boiling temperature of 60 apparent purity massecuite at saturation. The next gives

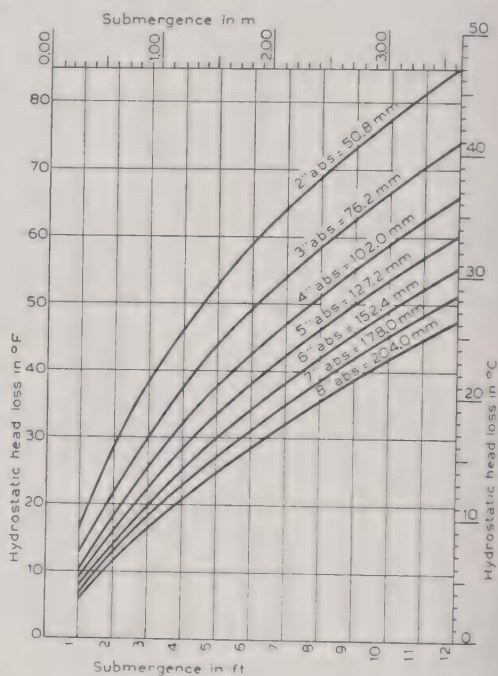


Fig. 11/11. Hydrostatic head temperature loss for massecuite boiling in vacuum pans.

the boiling temperature at a supersaturation of 1.325, the standard operating density.

To the temperatures indicated on the 1.325 supersaturation curve are added the temperature hydrostatic head losses corresponding to a submergence of 1 ft. (305 mm) for the various absolute pressures from 2" successively to 8", and this gives a new curve showing the boiling temperatures 2" (305 mm) below the surface of the massecuite in the pan.

In the same way similar curves are plotted for submergences of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 ft., with metric equivalents. Another detail in the picture is the temperature at which massecuite would drop down to the saturation point at various vacua. This is obtained from the b.p. rise chart (Fig. 11/10), and is as follows:

At 2" abs., saturation temperature is 164.5° F (73.6° C)

At 3" abs., saturation temperature is 185.5° F (85.3° C)

At 4" abs., saturation temperature is 215.0° F (101.6° C)

At 5" abs., saturation temperature is 235.0° F (112.8° C)

The dotted line shows the curve.

Finally, at the bottom of the graph are two horizontal lines representing the temperature of steam as it might be used in the calandria of the pan, one for 5 lb. (0.35 kg), and the other for 10 lb. (0.70 kg), giving steam temperatures of 227° F (108.3° C) and 240° F (115.5° C) respectively. These can be used to study the ΔT as affected by the hydrostatic head.

Interpretation

This graph sheds light on the elusive difficulties encountered in the satisfactory appraisal of the design and performance of vacuum pans.

Technologists agree regarding the limited height above the heating surface to which a strike of sugar can be carried with impunity, particularly C-massecuite which is the basis of the study. This depends upon the steam pressure and vacuum available, which determine the overall temperature difference at the heating surface, from which must be subtracted both the b.p. rise and the hydrostatic head loss of temperature, leaving the residual ΔT which makes the pan boil.

The maximum height above the calandria has been taken at 6 ft. (1.820 m). With tubes of usual proportions, 4" (101.1 mm) diam. and 4 ft. (1.220 m) long, a further note must be made. Since the temperature of the massecuite passing through the downtake approaches that at the boiling surface, it will always be necessary to do a certain amount of heating before ebullition

occurs. It was shown previously how slow is the velocity of this massecuite as it enters the tubes, and hence at this point the heat transmission will be low, and this will take an appreciable part of the heating surface. The lower the level of the massecuite, the less heating and the more boiling there will be; and the higher the level, the more heating and the less boiling. With turbulence incident to evaporation under vacuum, there will be violent motion in the tubes when the levels are low, and hence a much higher rate of heat transmission and evaporation.

An example would be interesting. Assume that the *C*-strike is being made at 60 purity, with steam at 5 lb. (0.35 kg) and a vacuum of 4" (101.1 mm) absolute. This corresponds to the third abscissa of the graph. The temperature at the boiling surface is 150° F (65.5° C). Upon reaching the bottom of the tubes of the calandria, the ΔT would be $227 - 150 = 77^\circ \text{ F}$ (42.7° C). If the massecuite were flush with the upper tube sheet, the b.p. here would be 150° F (65.5° C). At the bottom of the tubes, four feet below, with the corresponding submergence, it would be 182° F (83.3° C). However, the massecuite would have to be heated to this point before boiling. It is evident from this that in every case there must be heating in the tubes before boiling can take place, and inefficient heating at that.

The average of this temperature in passing through the tubes is 166° F (74.3° C) and the ΔT is 61° F (33.9° C). The other extreme would be when the massecuite is 6 ft. (1.830 m) above the calandria. In this case the boiling temperature at the bottom of the tubes would correspond to a submergence of 10 ft., giving 209° F (98.3° C), and at the top of the tubes it would correspond to a submergence of 6 ft. which gives 192.5° F (89.2° C). The average of the two is 200.7° F (93.7° C), so that the ΔT would be $227.0 - 200.7 = 26.3^\circ \text{ F}$ (14.6° C). In the other case, the average temperature of massecuite is 166° F and the ΔT would be $227 - 166 = 61^\circ \text{ F}$ (33.9° C).

If this massecuite actually boils at around 10° F above normal, not unexpected at high levels, the ΔT at the full strike will drop to 16.3° F (9.06° C), which is only 26% of the high point. For that reason it is not abnormal to find the rate of evaporation at the end of a *C*-strike only one-quarter of what it was at the beginning, and even less with adverse conditions.

This is certainly a sound argument in favor of the 'low head' pan in which the diameter of the liquor belt may be increased as much as 25%, which permits the strike to be made without having to go so high with the consequent loss of ΔT , and hence speed of operation, not to mention other objections. In many cases, instead of being satisfied with this improved situation, the massecuite height of 6 ft. (1.830 m) is still retained and a larger strike is made.

The dotted line is very interesting, and indicates that the point of un-saturation can be attained in a pan, wherein sucrose can redissolve into the massecuite, raising the supersaturation when again lower temperatures are attained with danger of additional nucleation. It is interesting to note that this situation is much worse with high than with low vacuum.

(n) *Temperature-Pressure Graphs for Refinery Strikes*

The graph (Fig. 11/12) is similar to the one just presented, but prepared for a purity of 100 corresponding to white liquor strikes in refineries whose

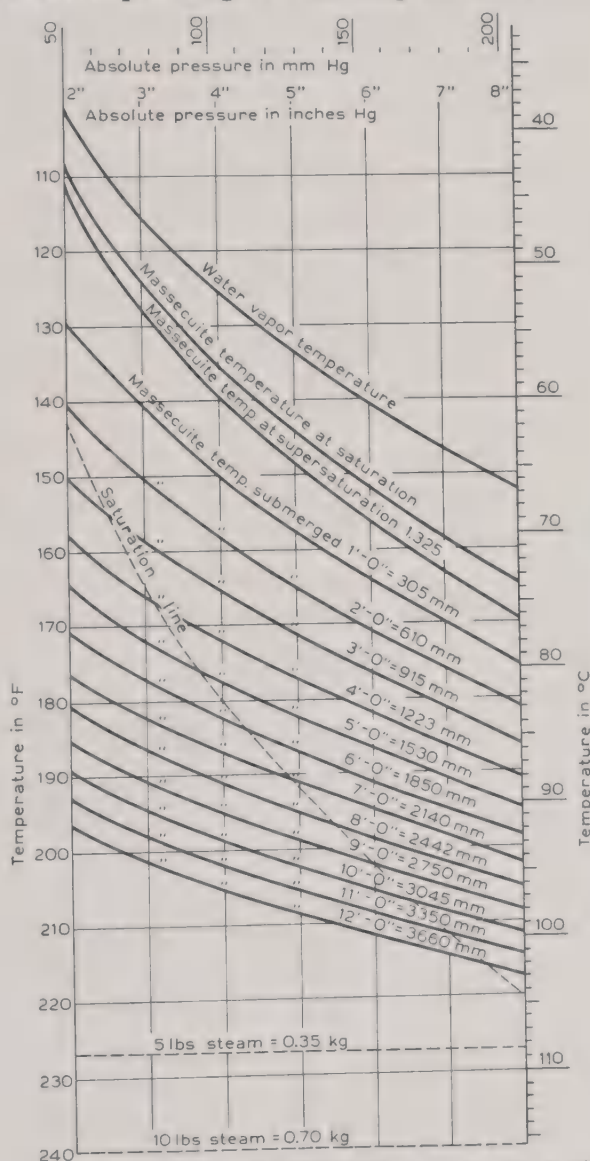


Fig. 11/12. Temperature-pressure chart for 100 purity massecuite boiling in vacuum pans.

purities approximate 99.4. Here the effect of reduced purities as sucrose is crystallized out of solution is practically negligible, because the purity of the run-off would drop only to about 98.5, and this has a negligible effect on the b.p. rise.

The first observable difference between the two graphs is that all temperatures other than for steam and absolute pressure are materially lower, due to the smaller b.p. rise incident to high purity, thus giving a greater available ΔT for operation, and consequently a faster rate of evaporation from this source alone.

A matter of special interest is the position and shape of the dotted saturation curve, which here acquires additional significance (Table 1).

TABLE 1

Absolute pressures	Saturation temp.	Submergence
2" equal to 50.8 mm	143° F eq. to 61.7° C	2.2 ft. eq. to 0.661 m
3" equal to 76.2 mm	165° F eq. to 73.9° C	3.8 ft. eq. to 1.162 m
4" equal to 101.2 mm	180° F eq. to 82.2° C	5.6 ft. eq. to 1.712 m
5" equal to 127.2 mm	191° F eq. to 88.3° C	7.2 ft. eq. to 2.200 m
6" equal to 152.8 mm	202° F eq. to 94.5° C	9.1 ft. eq. to 2.780 m
7" equal to 178.0 mm	212° F eq. to 100.0° C	11.1 ft. eq. to 3.390 m
8" equal to 203.5 mm	220° F eq. to 104.5° C	13.0 ft. eq. to 3.970 m

In this pan the massecuite level at the maximum point was 6'0" (1.825 m) above the upper tube sheet, and the tubes were 32" (0.813 m) long, so that the maximum depth possible for submergence during the strike was 8'6" (2.590 m).

Old time sugar boilers have always preferred to boil white sugar at low vacuum. One reason for this is the low viscosity of the fillmass. Another is that the crystals grow faster at higher temperatures. The graph indicates a third interesting reason, namely that at low vacuum, reversion to unsaturation is not possible. Since the maximum height of the massecuite is 8'6" (2.590 m) at absolute pressures of 6" or more, unsaturation would never occur, and this probably has a marked influence on the presence or absence of false grains and conglomerates. The assumed supersaturation is 1.325, as before, and if during the making of the strike there are deviations, the saturation temperature will change also either up or down.

(o) *Significant Observed Fact on Pan Temperatures*

In any calandria vacuum pan in operation equipped with a standard angle thermometer located 12 inches above the upper tube sheet, the observed

temperature at this point does not indicate that ebullition should be going on. It does boil, as evidenced by the considerable vibration when the proof stick is withdrawn to the mid-position. This situation has been checked in many vacuum pans and the result is always the same. It seemed worthwhile to investigate the point and throw more light on what goes on in vacuum pans.

(p) *Pan Temperature Investigations*

The writer was given the opportunity to conduct an extensive series of investigations on the subject of pan temperatures at Centrals Boston and Weston of the United Fruit Company in Cuba in 1930. A summary of the results was presented before the Process Division of the American Society of Mechanical Engineers in 1934, and some of the data are included in the discussion that follows.

The work was limited to a determination of temperatures at the top of the tubes, while other pertinent data were recorded for correlation. To make the observations, the equipment shown on Fig. 11/13 was mounted on a 2'0" vacuum pan having 5" No. 14 copper tubes 4 ft. long and a 72" downtake. First, a tube was selected as near the shell of the pan as possible, and a ferrule was inserted into it extending vertically 6" above the tube sheet. Then, an accurately calibrated Clerget thermometer was selected giving readings in tenths of °C and mounted in a proof stick made up of a 3/4"

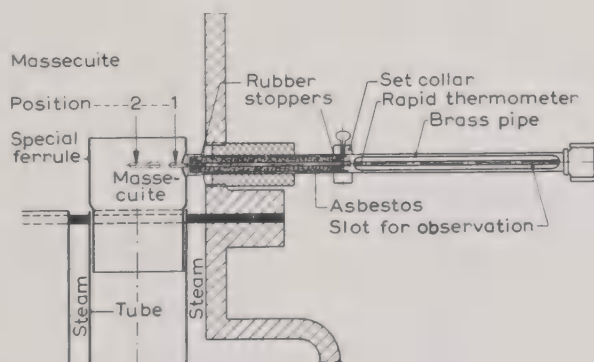


Fig. 11/13. Experimental thermometer for reading local temperatures in tubes of calandria pans.

brass pipe with the sensitive bulb sticking out of the end through a rubber stopper, closing the pipe against leakage. A slot was made in the 3/4" pipe in the part projecting outside the pan, thus making it possible to take readings. A 1 1/2" hole was tapped in the shell of the pan and a short piece of brass stock was screwed in. In the centre of this 1 1/2" plug was provided

a $3/4$ " plus clearance hole for the free passage of the proof stick with its thermometer. The hole in the pan was made exactly in line with the centre of the 5" tube prepared for observation. A hole was made in the ferrule, allowing the thermometer and its mount to pass freely, so that the sensitive bulb could be located at any desired position in the range.

(i) *Observation procedure*

An adjustable set collar with a set screw was fitted to the proof stick thermometer outside the pan with calibrated wooden blocks for insertion between the plug and the set collar, thus permitting the placing of the sensitive bulb of the thermometer at the three agreed points of observation: (1) in the centre of the tube, (2) at the inner periphery and (3) entirely outside the tube. The sensitive bulb of the thermometer was about $7/8$ " long, and thus it was impossible to record the temperature exactly at the centre of the tube or exactly at the inner periphery, which constituted unavoidable limitations.

A standard procedure was used in making the observations in the three positions. In all cases the instrument was allowed to remain at each station two minutes, with readings every ten seconds, after which an interval of one minute was taken for making other observations on the pan, including the steam pressure, the temperature at the standard angle thermometer, and the height of the massecuite above the upper tube sheet, so that all this information could be correlated. The graphical log of the results is given (Fig. 11/14), and is worthy of careful consideration.

(ii) *The results*

Thousands of temperature readings were made at the experimental thermometer, and whereas only one graph (Fig. 11/14) is given here, a number of tests were made on other pans of different proportions and operating conditions, but all gave similar results, subject to the same interpretations.

The readings of the experimental thermometer fluctuated wildly and were difficult to make. At the beginning, with low massecuite levels, vigorous boiling was going on in the tubes, and the temperatures at station 1 were consistently higher than at the other positions, but excessive turbulence made it hard to get fair readings. At this stage, the temperatures shown by the experimental thermometer at all stations were always higher than that at the pan angle thermometer against which it was checked.

The maximum difference between the two instruments was about 7°C (12.6°F). The difference between adjacent stations of the experimental thermometer was not great, 1 or 2°C (3.6°F). This situation is due to the very turbulent condition in the tubes at the location of the thermometer, resulting in a fairly good mixture approaching uniform temperature.

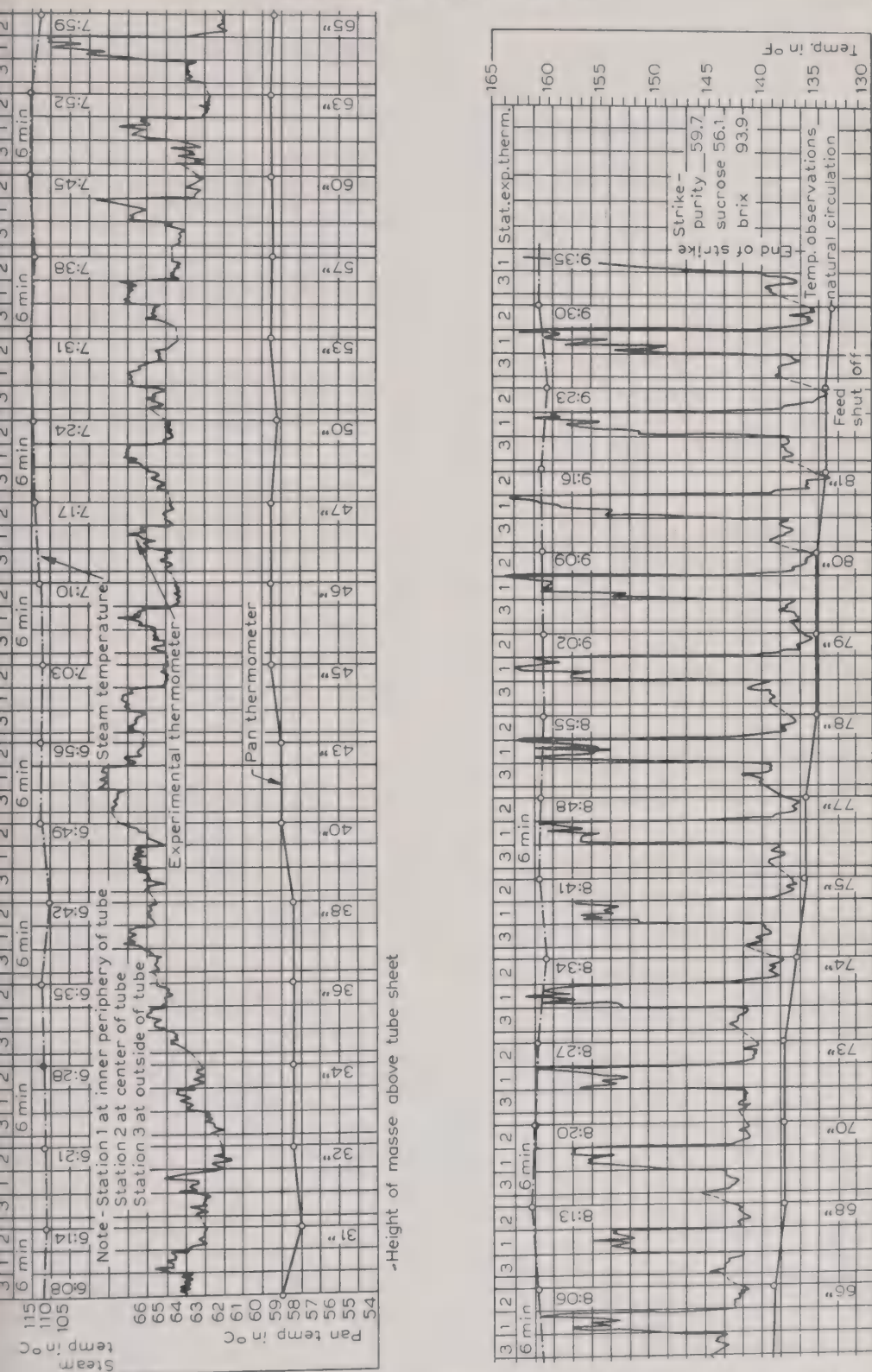


Fig. 11/14. Local temperatures in tubes of calandria pans with natural circulation.

As the strike proceeds, the temperature at the inner periphery of the observed tube increases more and more, and that of the other two stations approaches that of the pan angle thermometer, actually equalling it towards the end of the strike. The maximum observed difference between the experimental thermometer at the inner periphery of the tube and at the centre is of the order of 17°C (30.6°F). Bearing in mind the instrument limitations, it is evident that this difference must be greater than observed; and it is the present interpretation that what determines this is the superposed hydrostatic head of massecuite at the point and time of observation. See graph (Fig. 11/10).

At the last reading the vacuum was 27.2" at sea level (683 mm) and the absolute pressure was 2.8" (71.1 mm), giving vapor temperatures of 111°F (44°C); while the angle thermometer showed 133.5°F (56.5°C), giving an apparent b.p. rise of 22.5°F (12.5°C). The purity was 60.0, and hence this seems subnormal by a considerable amount, even if this angle thermometer happened to be in contact with some of the unheated massecuite leaving the top of the tubes due to very slow evaporation at this stage. Actually, the height of the massecuite over the experimental thermometer was 76" (1.93 m). At the brix of 94 recorded, massecuite weighs 94 lb. per cu.ft. and this corresponds to a loss of vacuum due to hydrostatic head of 8.43" (214 mm). Adding the absolute pressure corresponding to the vacuum, we have at the experimental thermometer 11.3" (287 mm), and the vapor temperature corresponding to this is 166°F (74.5°C). Subtracting the pan vapor temperature from this gives 55°F (30.6°C) so that by adding this to the boiling temperature at the surface of the massecuite (estimated at 131.5°F (55.4°C)) the probable boiling temperature at the experimental thermometer would be 186.5°F (85.8°C) instead of the 165°F (74°C) observed, a difference of 21.5°F (11.95°C) above the recorded one.

(iii) *Outstanding fact*

The outstanding fact established by the investigation is that the massecuite upon leaving the upper ends of the tubes of calandria pans is not uniformly heated at all. Local variations may reach as high as 50°F (31.2°C) at the end of the strikes, and possibly somewhat more inside near the top of the tubes. This variation will be much less when the height over the tubes is lower.

(iv) *What is the significance of this?*

There follows an appraisal of the significance of these facts and their influence on vacuum pan operation.

What causes circulation in vacuum pans? When the level of the strike

low, circulation is induced by the formation of vapor bubbles in the tubes of calandria pans or at the heating surfaces of others, thus reducing the specific gravity of the mixture of vapor bubbles and massecuite as against massecuite alone, free of bubbles in the downtake. The difference in weight of these two columns causes upflow in the tubes and in the outer periphery of the pan, and downflow in the downtake. This is circulation. It has been claimed that circulation takes place by convection due to the fact that massecuite is hotter at the heating surface and above it than in the centre of the pan and the downtake, where there is no heating surface. It is hard to conceive of any force brought about purely by temperature differences of the magnitude known to exist that would be adequate to cause appreciable movement of the heavy viscous massecuite. It is easy enough to estimate the value of this force as a maximum.

If the foregoing were true, then the maximum circulation would take place at the end of the strike, when the levels are high, and this is not the case. Taking a pan with massecuite 6 ft. (1830 mm) above the upper tube sheet as an example, consider the following.

The pan thermometer during the test above read 59°C (138.2°F). It is also known that the minimum temperature at the boiling surface was about 55.2°C (131.5°F), since the vacuum was 27.3" when the observation was made. The minimum temperature in the downtake on the average could not be less than that. The difference is therefore 6.7°F (3.71°C).

Assumed further that the change of temperature in the tubes is gradual throughout their length, we can therefore say that we have two columns of massecuite 8 ft. (2440 mm) high. The expansion due to this difference of temperature is 0.39%. In other words, the difference in head between the two columns would be 0.39% of 8 ft., which is 0.0312 ft., or 0.374" as an absolute maximum. Actually through the tubes themselves it would not be more than one-fourth of that figure. It is totally beyond the realm of possibility that such a small difference of pressure would have any effect whatever on the movement of the thick viscous massecuite, and therefore the hypothesis must be completely abandoned.

(q) *The Real Mechanism of Natural Circulation*

It has been established above that massecuite, as it leaves the tubes of the pan on its way up, is not uniformly heated, but, on the contrary, contains many spots at different temperatures, the general average of which is roughly represented by the readings of the pan thermometer, the spread between the maxima and minima attaining the astonishing value of as

much as 50°F (27.8°C). As the mass proceeds upwards, even in the tubes themselves when these spots reach the level where the local vacuum as reduced by the hydrostatic head corresponds to the boiling temperature of the hot spot, a flash takes place with the release of a vapor bubble whose size corresponds to the magnitude of the hot spot. The volumetric displacement resulting from this causes a sudden readjustment of position, permitting the vapor so liberated to come into contact with some of the cooler massecuite, when immediate condensation takes place.

This procedure is repeated on the way up, gradually lowering the temperature of the hot spots by raising that of the cold spots, through these little explosions and condensations, ultimately attaining the general average temperature indicated by the pan thermometer. This average exists in uniformity at the level of uninterrupted ebullition, probably limited to a zone extending 12" below the surface of the massecuite in the pan. There is no doubt that this is the formula of natural circulation in vacuum pans, for whereas the individual displacements are small in volume and duration, they are infinite in number and extend from the tubes themselves to the top of the massecuite. As fast as one flash bubble condenses, another takes its place nearby. It can be seen that the weight of this vapor-charged, agitated massecuite in the outer periphery of the pan is lightened as compared with the downward moving central stream which is free from flash spots.

Interesting Revelations

It must be noted that these intense volumetric disturbances caused by the flash explosions in no way injure the operation of the pan. Quite the contrary, they cause a continual rapid change of position of the sugar crystals in their surrounding molasses or syrup, thus permitting a more complete exhaustion.

The high temperatures involve the danger of inversion and color increment, particularly in view of the presence in the molasses of considerable proportions of heat-sensitive glucose. Another item is the fact that unsaturation may be reached in which sugar can redissolve into the molasses, thus raising its supersaturation, with the danger of provoking the formation of conglomerates and fines, not to mention a retardation of crystallization.

(r) *Conductivity of Massecuite*

Having our special equipment for making the observations, it was appropriate to see what could be found out regarding the heat conductivity of

massecuite under operating conditions in vacuum pans. Whatever could be done would be on full scale under actual operating conditions, and would reflect what might be expected with the handicap of high viscosity and concentration regarding the transfer of heat.

A standard C-strike was boiled until the level of the massecuite was 1 ft. above the upper tube sheet. Then steam was shut off and vacuum dropped and the readings of the experimental thermometer were continued, but this time using stations 1 and 2 only. The idea was to find out how long it would take for the temperature at the inner periphery of the tube to equalize with that at the centre. As in the former test, the thermometer was kept at each station for two minutes, and readings were taken every 10 seconds. Fig. 11/15 shows the results, indicating that it would require at least one hour for these temperatures to equalize.

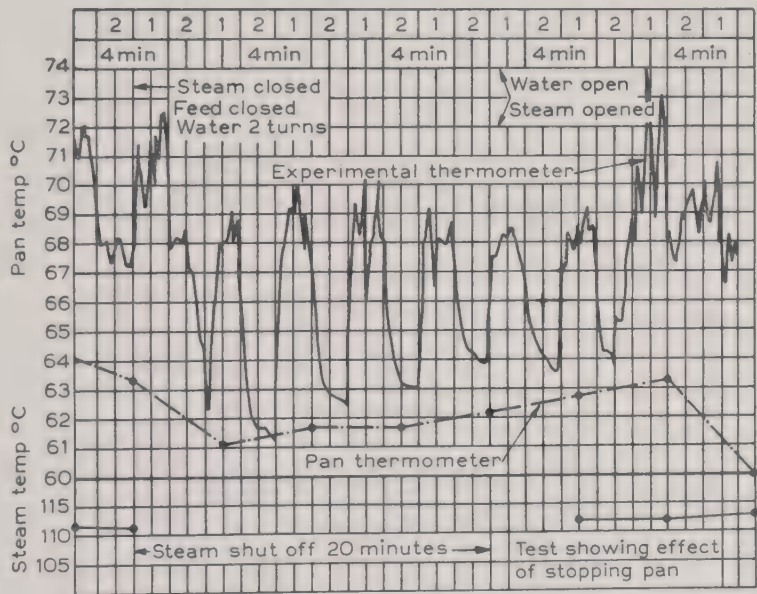


Fig. 11/15. Effect of viscosity on heat penetration through massecuite in tubes of calandria pans.

This must have considerable significance on performance. For one thing, it is evident that until boiling takes place in the tube, the transfer of heat is excessively slow, and there is a skin heating effect with the centre of the cream unaffected. With this in mind, it is easy to reconcile the facts as shown in the graph of the previous test. Evidently, this condition obtains in all vacuum pans, and if so, it calls for some remedy to overcome the difficulty – and this remedy is *mechanical circulation*.

2. The Rehabilitation of Mechanical Circulation

(a) *Introduction*

The idea of mechanical circulation in vacuum pans is very old. There have been many designs tried all over the world and in almost every case the results have been disappointing, and their use has not been justified considering the additional cost and complication. An outline of a few such designs is given below.

(b) *Old Circulators*

Probably the first circulator used in vacuum pans in the sugar industry was the original German GROSSE apparatus, which consisted of a section of screw conveyor installed in the downtake space of coil pans, overlapping the height of the coils and extending below near the discharge valve. The

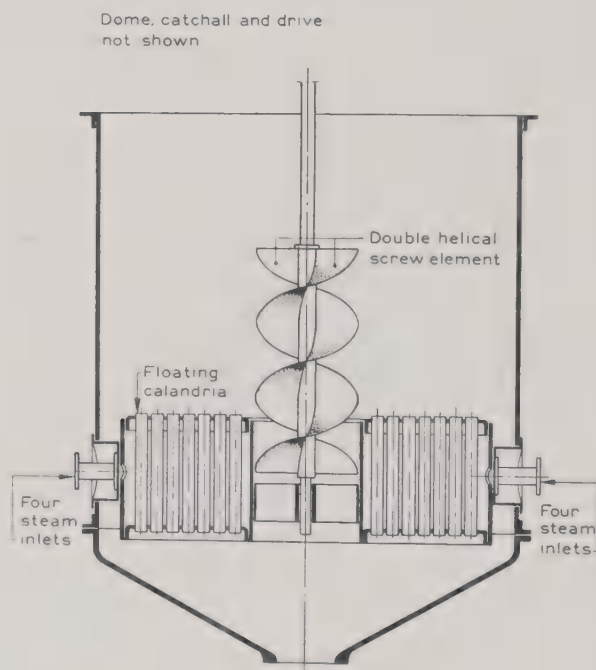


Fig. 11/16. FREITAG circulator in pan with floating calandria.

idea was that by this arrangement forced circulation would be operative from the very beginning to the very end of the strike. This design was used in the beet sugar industry, and is no longer in service to our knowledge. It is now generally agreed that mechanical circulation is of little benefit in coil pans.

a more recent design, until lately built by the CAIL Co. of France, was known as the FREITAG apparatus (Fig. 11/16). This also consisted of a segment of screw conveyor, projecting into the downtake of a floating calandria pan, and extending upwards to a point slightly below the massecuite level. The diameter of the conveyor was about 25% of that of the pan, and that of the downtake enough larger to provide working clearances. Unfortunately, with a floating calandria there is a handicap due to the fact

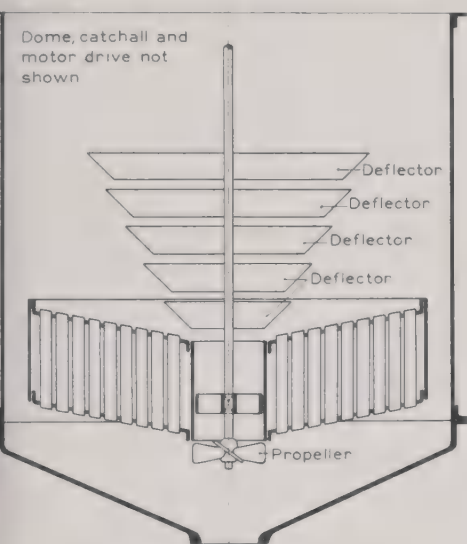


Fig. 11/17. Helico-agitator by QUINT and FLAMANT.

that the annular space between the shell and the calandria offers much less resistance to the passage of circulation than the tubes, so that a large part of the displacement of the circulator by-passed the heating surface and lost its usefulness as far as forced circulation is concerned.

Still another French design is the HELICO-agitator (Fig. 11/17), consisting of a small propeller about 18% of the pan diameter, likewise installed in a floating calandria pan, and suffering similar defects to those outlined above. The new part of this design is the succession of superposed inverted funnels above the downtake, increasing in diameter until the uppermost, just below the massecuite level, attains perhaps 60% of the pan diameter. Due to the small size, the power requirements must be very low, and its ability to move a large amount of massecuite for even fair circulation is inadequate.

(c) *Necessity of Mechanical Circulation*

In spite of all past inadequacies clearly indicated by absence of extensive applications, the fact still remains that the analysis of velocities of massecuite circulating through heating surfaces of pans in operation, even those designed especially for easy flow, emphasizes the urgent necessity of adequate forced movement to obtain fair performances. This applies not only on the basis of rates of evaporation and crystal growth, but also to minimize temperature conditions involving danger of heat injury to the products. This was all detailed in the preceding discussions.

(d) *Basis of Design*

With the above background in view it was decided to embark on a development project to solve the problem. As indicated by a review of previous work, it is evident that the units tried were too frail, had too little capacity, and were inadequately powered. The new design was planned to fit the calandria pans used in our study. The selected speed through the tubes was taken at $1\frac{1}{2}$ ft. (457.0 mm)/sec, corresponding to the calculated values with natural circulation while the levels are low and the performance satisfactory.

(i) *Data for experimental circulator*

The pan was 12'0" (3.660 m) diameter, provided with 306-5" (127 mm) tubes, 48" (1.220 m) long, making up a total of 1600 sq. ft. (149 sq.m). The downtake was 6'0" (1.825 m). The tubes had been selected 5" diameter to minimize friction and produce free circulation. The price paid for this was a material reduction of heating surface. The strike capacity was 1300 cu.ft. (370 hl), so that the heating surface to massecuite ratio is relatively

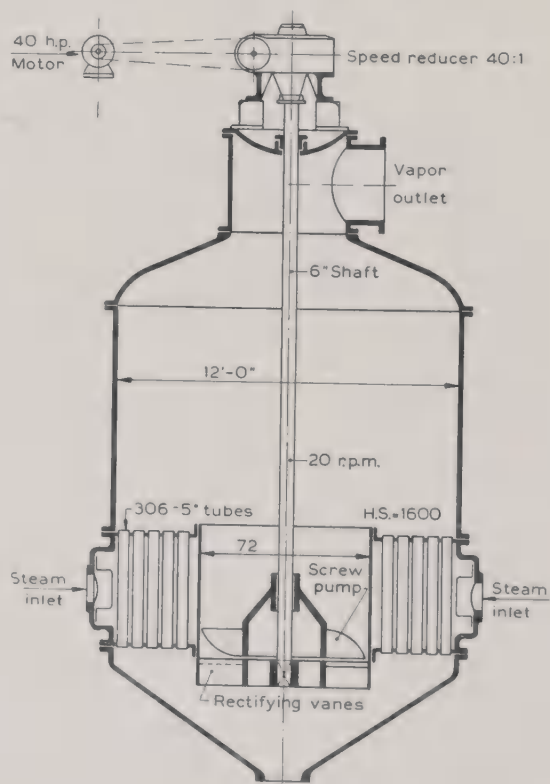


Fig. 11/18. Original vacuum pan with experimental circulator at Central Boston in Cuba.

ow. There were three such pans in the sugar factory, so that it was easy to make direct comparisons of performances.

The inside area of a 5" No. 14 tube is 18.35 sq. in., or 0.127 sq. ft., and the total area for the 306 tubes was 39 sq. ft. (3.630 sq.m). The area of the 2" downtake was 28.3 sq. ft. (2.64 sq.m). To give a velocity of circulation of 1 ft. per second in the tubes, the volume of massecuite must be 39 cu. ft. (11.05 hl)/sec; and for $1\frac{1}{2}$ ft./sec, it must be 58.5 cu. ft. (16.5 hl)/sec.

The circulator (Fig. 11/18) consisted of a 70" six-element screw pump with a hub 36" diameter and a pitch of 72", and was planned to run at 30 r.p.m., at which the swept volume would be 58.95 cu. ft. (16.7 hl)/sec, giving just about 1.5 ft./sec in the tubes. Twelve rectifying vanes were provided below the runner. The drive was a 40 h.p. motor belted to a worm gear speed reducer having a ratio of 40 : 1. When the circulator was started, both the gear and the motor were overloaded when the final concentration was given, and it was necessary to slow down from 30 to 20 r.p.m., and all tests were made at that speed. To reduce friction, half the rectifying vanes were removed, using only six. Subsequently, it has been established that these vanes do very little good, and increase substantially the power to operate.

(ii) *Displacement data*

There were no available means of making measurements of capacity. The actual shut-off head was determined by operating the circulator with the pan empty and gradually admitting water until the level was just flush with the tops of the tubes, when a measurement was made of the depression of the water level in the downtake. This proved to be the ridiculously small amount of 6" (152.5 mm). It was concluded therefore that the capacity of the screw pump was inadequate for our purposes. However, to change this would involve the loss of one year, and it was decided to proceed with the tests. At the reduced speed, the horsepower developed while making a strike but before bringing it together was only 12 at 20 r.p.m. on the circulator.

(iii) *Difficulties*

In the first runs made, the apparatus showed promise. The difficulty was that temperatures above the calandria were always abnormally high, indicating that a considerable part of the massecuite in circulation did not reach the boiling surface and shunted back to the downtake without releasing its superheat by flashing, as it should. To overcome this, a screw

element was attached to the circulator shaft 24" above the calandria and extending 3 or 4 ft. higher. This reduced the undesirable temperature increment, and in subsequent designs modifications were made to capitalize on this fact.

(iv) *Further developments*

Since the original installation, the apparatus has undergone considerable alterations. First, a framework of containing rings was mounted above the downtake with screw elements with rectifying vanes between each, and a number of units were built with this modification. The amount of head developed by the screw pump indicated the necessity of increasing the speed and reducing the diameter. It was finally decided to make all circulators and downtakes 40% of the pan diameter, and these proportions have remained to this day.

The peripheral speeds at the tips of the screw vanes have been standardized at about 16 ft. (4.880 m)/sec. The early models after the first trial had the main impeller just inside the downtake to reduce the shaft length. It was later found that a major improvement could be achieved by placing the screw pump just below the downtake, eliminating all rectifying vanes and other screw elements, and this is the present status of the design. The arrangement approaches a mixed flow pump, which is more suitable to the work, as the elements of the screw are self-clearing when the viscosity is high, and there is less friction, more capacity and less power required (Fig. 11/19).

Until recently there was still a tendency to shortcircuit the boiling surface of the massecuite, which was the original difficulty, but this has been overcome by the addition of a funnel-shaped deflector at the top of the downtake with an angle of 45 degrees and a height of 8". The effect of this is about the same as having a larger downtake without losing heating surface. One advantage is that the path of the heated massecuite leaving the tubes veers away towards the shell of the pan, thus concentrating the

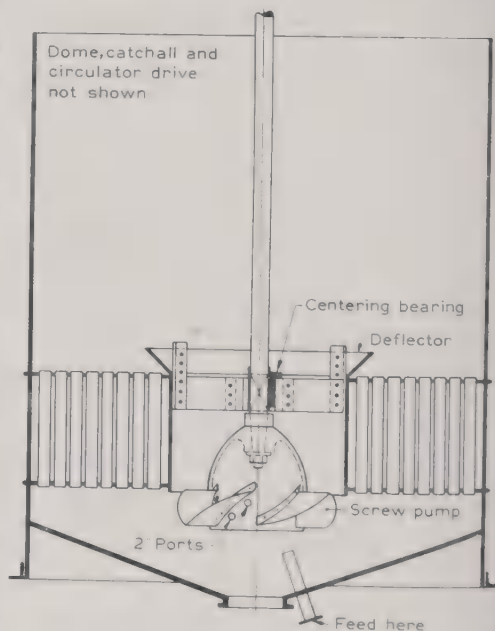


Fig. 11/19. WEBRE mechanical circulator as presently built.

one of ebullition at that point, leaving the centre free from boiling, and permitting the massecuite after flashing to proceed downwards with little interference from rising currents of hot material from below.

(y) Feed control

Having only one rotor to the circulator in the bottom of the pan, where it is always submerged, means that the power required to drive it will always be proportional to the tightness or viscosity of the massecuite, and a wattmeter attached to the driving motor circuit will give indications that are exactly proportional to tightness. This is really the control element for operating vacuum pans after the initial period of footing preparation, and any sugar boiler, by simply reading the wattmeter can feed his pan accordingly. This is so true that today circulator pans are equipped with automatic feeding systems simply devised by using a contacting wattmeter whose signals open and close the feed valve, thus requiring no attention except to attain final concentration, when the feed must be closed and the final brix judged by the indication of the wattmeter. There are now many such installations in raw sugar factories and refineries.

Another interesting feature is the way feed is dispersed into the pan. The incoming liquor is admitted into the bottom, and guided upwards towards the inside of the hollow hub to which the screw elements are bolted. Under each vane are two 2" (50 mm) holes through the hub, and feed is made to enter the system here under the rapidly revolving vanes, where it is immediately and thoroughly mixed with the circulating massecuite, very much better than it has ever been done before.

A useful operating detail is the standardization of the control of feed to the pan. It has been established that the best tightness at which to carry the strike is by holding the load on the wattmeter at 75% of that developed at the final concentration. This is simply obtained by noting the final load on the wattmeter when the wanted brix is attained, and on subsequent operations set the contact for feed control at 75% of this load.

(e) Speed and Power Requirements

The power required to drive vacuum pan circulators of the present design varies considerably with any specific size, according to the kind of massecuite being elaborated, and especially with the brix and viscosity, the latter depending on the composition of the impurities in the massecuite. The worst job of all is to handle low grade remelt strikes in sugar refineries, and it is necessary to increase the power by 25% above the standards

given below. Low raws in the beet sugar industry also need the same increase in power, especially after the beets have been stored for a long time and the raffinose content has increased beyond normal. The following are the present standards (Table 2).

TABLE 2

Circulator diam.	R.p.m.	H.p.
66" (1.68 m)	55	60.0
60" (1.52 m)	60	50.0
54" (1.37 m)	67	40.0
48" (1.22 m)	75	30.0
42" (1.07 m)	86	25.0
36" (0.91 m)	100	20.0

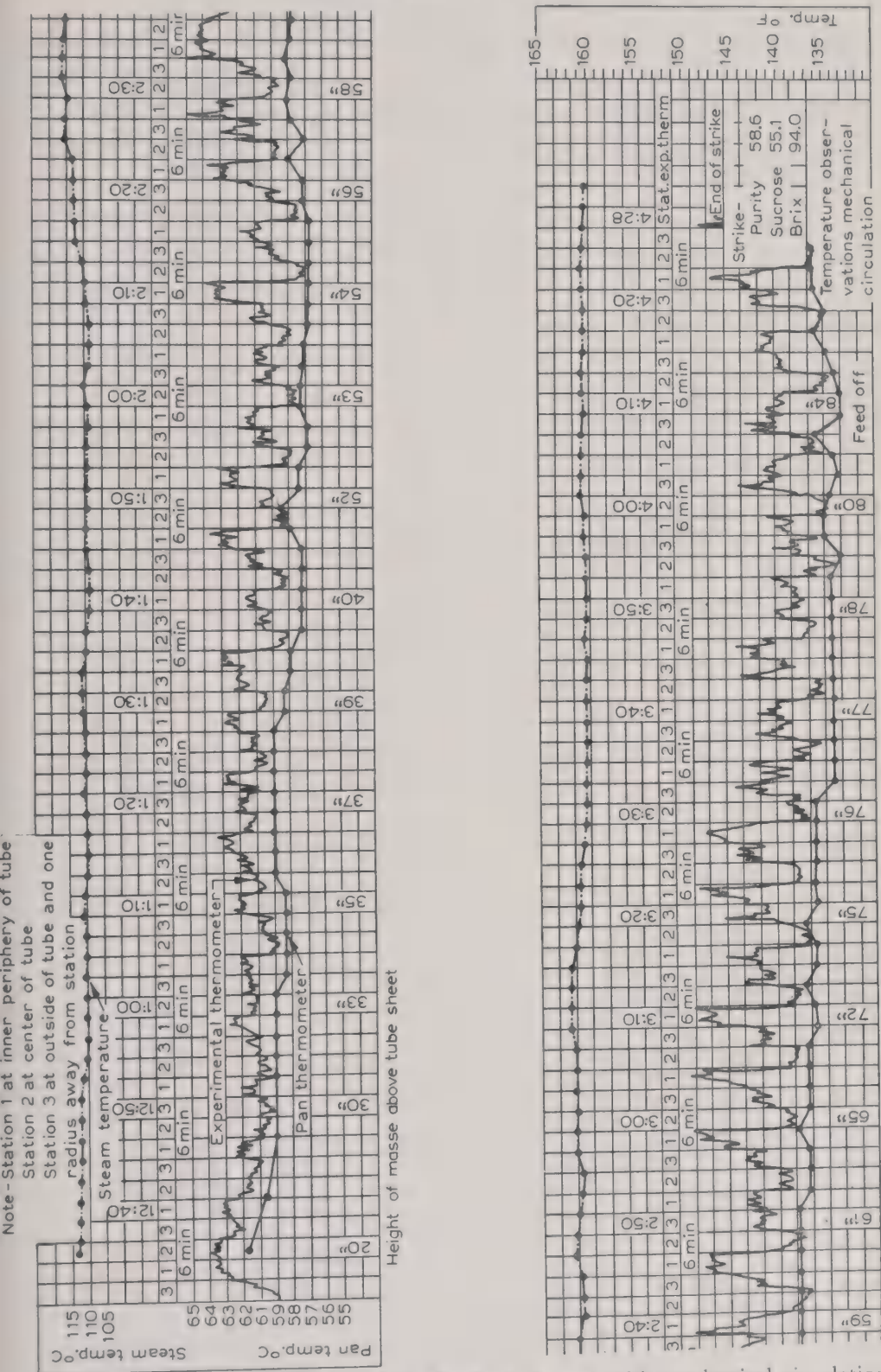
The maximum power loads will occur when the strike is given its final brix, and if it has been carried at 75% of the dropping load, as suggested, the increase of power at that point will be 33%. The duration of final concentration from the time feed is shut off to the end of the strike will not exceed 15 minutes. On white sugar strikes, this period is only 2 minutes. In view of this, the motor can accommodate a load of 25% in excess of rating without difficulty. When the pan is stopped, the circulator must be stopped immediately, because without change of brix the absence of ebullition alone will increase the load materially. There is more danger of injury to the speed reducer than to the motor, since heavy overloads beyond the manufacturer's rating may break down the film of lubricating oil between the gear teeth and result in serious damage.

(f) *Benefits of Mechanical Circulation*

(1) The apparatus used to measure the temperature conditions in pan No. 2 at Central Boston in Cuba was transferred to pan No. 3 which was equipped with the original experimental circulator, for the purpose of duplicating the observations and recording the results. Whereas this unit represented a preliminary design without refinements and corrections, still there developed notable differences worth considering.

The graphical log of the observations is reproduced here (Fig. 11/20). The experimental thermometer and the pan thermometer gave readings very close to one another at the beginning, but towards the end the difference between stations 1 and 2 inside the tube reached a maximum of only 11° F (6.1° C) instead of 31° F (17.2° C) recorded in the first test, which is a considerable improvement.

(2) With the original design of mechanical circulation, it was possible



to operate the pan with low temperature vapors under partial vacuum, and a test was actually recorded while making a *B*-strike in which the pressure was always sub-atmospheric. Below (Table 3) are given summaries of three tests made with and without circulator.

TABLE 3

Nomenclature	Pan 2- <i>C</i>	Pan 3- <i>C</i>	Pan 3- <i>B</i>
Steam pressure	6.28 lb.	2.99 lb.	2.0 in. vac.
Vacuum	28.30 in.	28.00 in.	27.5 in.
Steam temp.	230.5 °F	221.5 °F	208.6 °F
Massec. temp.	132.9 °F	139.0 °F	132.3 °F
ΔT	97.6 °F	82.5 °F	76.3 °F
Heat trans. <i>U</i> .	37.6	57.6	64.0
Max. evap.	10880 lb.	12120 lb.	17750 lb.
Min. evap.	838 lb.	2810 lb.	2870 lb.
Average evap.	5675 lb.	7330 lb.	7570 lb.
Evap./sq. ft./h	3.54 lb.	4.58 lb.	4.73 lb.
Total evap.	38700 lb.	46300 lb.	58100 lb.
Time required	6 h 48'	6 h 20'	7 h 30'

Today these data are obsolete, because with a circulator pan under the same conditions it is possible to make a *C*-strike in two hours. They are given for comparison of what was possible then and show the progress.

(g) *Comparative Rating Curves*

In 1940 at Central Aguirre in Puerto Rico, parallel tests were made on *B*-strikes on two pans exactly alike, one with a circulator and the other

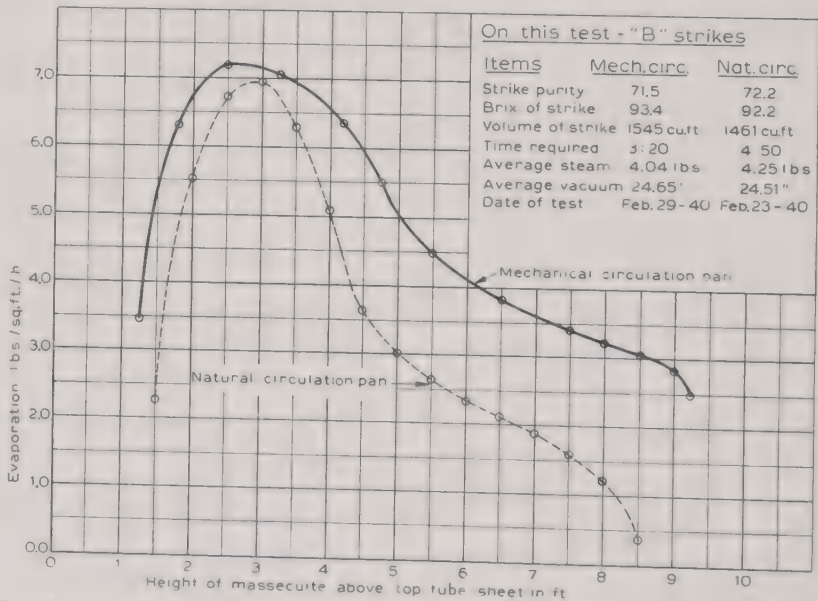


Fig. 11/21. Comparative rates of evaporation in *B*-strikes made with and without mechanical circulation. For both pans: diam. = 12'0", downtake = 48", tubes = 621 - 4" x 54" copper, h.s. = 2860 sq. ft., rating = 1500 cu. ft., footing = 500 cu. ft.

without. The results are shown in the graph (Fig. 11/21). These two runs were made by the same sugar boiler under nearly equal conditions, but it was not possible to maintain exact duplication in all respects, and the operating conditions favored the pan without circulator because the final brix was lower by 1.2, the purity was higher by 0.7, and the volume of massecuite made was less by 84 cu. ft. The other conditions were about equal. The big gain here, as always, is towards the end of the strike with mechanical circulation.

The graph shows the rate of evaporation in lb./sq. ft./h. The peak occurred at the fourth observation and is about equal for the two pans, so that practically nothing was gained by mechanical circulation at the beginning. Summarizing, the following is of interest (Table 4).

TABLE 4

Height above cal.	No circulator	Circulator	Gain %
1 ft. (305 mm)	—	—	—
2 ft. (610 mm)	5.50	6.70	22%
3 ft. (915 mm)	6.90	7.20	4.5%
4 ft. (1225 mm)	5.10	6.60	29.2%
5 ft. (1525 mm)	3.00	5.10	70.0%
6 ft. (1830 mm)	2.30	4.15	80.5%
7 ft. (2135 mm)	1.85	3.80	105.0%
8 ft. (2440 mm)	1.20	3.20	166.0%
Last	0.40	2.50	525.0%

The duration of the circulator strike was 200 minutes against 290 minutes, which is 69% of the time. If this is corrected for the larger volume, the figure becomes 65.2% of the time without circulator. The rate of evaporation at the end was 0.4 lb. for natural circulation against 2.5, which is about six times as fast for the circulator when the temperature and viscosity are greatest — quite a significant advantage. If this were a low grade strike of about 60 purity, the time to complete a strike of equal volume with the circulator pan is about one-half that required for the pan without circulator.

(h) *Quality of Crystals*

It is generally admitted that conglomerates occur much more readily with high purity liquors. The effect of mechanical circulation of refinery liquors on crystal formation is shown in a microphotograph (Fig. 11/22) at a magnification of $10 \times$. The large grain is 'sanding sugar', made on a circulator pan; and the small grain is ordinary fine granulated sugar. The purity

of the while liquor in both cases was around 99.4. Both samples date back to 1954, and it is felt that these photographs speak for themselves.

(i) *Summary*

After twenty-seven years and the building of about one hundred and



Fig. 11/22. Micro-photographs of refined sugar crystals, made with and without mechanical circulation. Left: fine granulated crystals, 10 : 1, made in calandria pan with natural circulation. Right: sanding sugar crystals

seventy circulators, the following characteristics have been well established.

- (1) The time required for boiling ordinary cane sugar raw strikes has been reduced as follows: *A*-strikes 15–20%; *B*-strikes 25–30%; *C*-strikes 40–50%.
- (2) The rate of evaporation at the end of *C*-strikes is about six times as fast, but not different at the beginning.
- (3) The velocity of circulation in the tubes is about constant at 1.50 ft. (457 mm)/sec.
- (4) The estimated time of contact of massecuite with the heating surface is less than 3 seconds.
- (5) The maximum temperature attained in the tubes is considerably reduced.

-) The crystal formation is incomparably better.
-) The color increment is reduced.
-) Automatic feed is easily applied.
-) The displacement of circulators is great enough to turn over the entire contents of the pan about three times per minute.
- 0) Since circulation does not depend on evaporation, it is possible to feed with syrup or molasses just below saturation with impunity.

3. Equipment and Operating Conditions for Satisfactory Vacuum Pan Performance

(a) *Introduction*

In the not very distant past and in some places even now, the control of vacuum pans has been in the hands of practical operators using guesswork and the rule of thumb, learned from their predecessors and handed down to their apprentices as a craft with resistance to all change and progress. Since this is one of the most important steps in the manufacture of sugar, and since well established scientific knowledge on the subject is available, this practice can no longer be tolerated. It is now proposed to outline not only the equipment needed, but the way to use it.

(b) *Stable Conditions*

Satisfactory sugar crystallization is not possible with unstable conditions of operation, so the first requirement is to make adequate provisions in this respect.

(c) *Vacuum Control*

Each vacuum pan should have its own independent condenser that can be adjusted without interference from others. It would be desirable to have independent vacuum pumps, since moderate cost steam jet units are available. Usually there is one central water injection system of ample capacity serving all units.

A very good investment is to provide the condensers with automatic vacuum control based on adjustment of water supply to the desired vacuum. Thus equipped, there will be no changes of temperature due to vacuum variations, which is the most important step.

(d) *Stable Steam Pressure*

The pressure of steam fed to the heating surface of the pan must not be allowed to oscillate, as this will introduce another undesirable variable which

will influence the performance adversely. To obtain this, automatic controls must be provided to regulate steam in the lines, either relieving it to the atmosphere if too high, or admitting make up if the pressure tends to drop.

(e) *Instrumentation*

To be able to exercise proper control, there must be provided instruments to make this possible. Usually the temperature of the massecuite is indicated by an angle thermometer located low enough to be submerged at all times. There should also be a mercury vacuum gauge, and preferably an absolute pressure gauge. Then a steam gauge indicating the pressure at the heating surface of the pan is required. A water gauge glass must be provided indicating the level of the condensate inside, to make sure it is being removed.

All standard accessories must be included, such as sight glasses, manholes, discharge valve, water sprays, steam out, and a good scale must be mounted on the pan indicating the volume of the massecuite at different levels, so that proper blends of ingoing products can be made.

A very important detail is the design of the feed pipe, to make sure that the incoming liquor is well distributed into the mass. Lacking this, it is easily possible for the lighter incoming feed to stratify on the upper surface of the massecuite, which would spoil the operation (Fig. 11/1).

(f) *Supersaturation Control*

All pans must be provided with reliable instruments which will give the concentration for all purities and temperatures ranging from below saturation to about 1.80 supersaturation, preferably with indications of the location of the operating zone arbitrarily fixed at between 1.25 supersaturation and 1.40.

(g) *Steam Flow Meter*

Little appreciated but of great usefulness is having a reliable flow meter on the steam connection to the pan. The manner of using the indications for the control of liquor feed will be explained later.

(h) *Crystallization*

In raw cane sugar factories, grain is made for the low grade or *C*-strikes only, the other strikes beginning with footings of magma made of *C*-sugar mingled with syrup, clarified juice, or even water, this footing being large

nough to cover the heating surface. The operation is then completed using syrup or molasses in varying proportions or of various purities, according to the type of strike desired.

In sugar refineries, grain is usually made for each strike individually.

In beet sugar also, grain is made for each strike. All of the low raw sugar is melted and mixed with run off from the white strikes to make high raws. The white strikes are made from thick juice from the evaporators to which has been added all of the high raw sugar after it has been melted.

Thus in all sugar factories and refineries it is necessary to make grain by one of the three methods outlined below.

c) Letting the grain come in

The original system of making grain was to concentrate the syrup or liquor until the point was reached where nucleation took place spontaneously, and continue with evaporation until a proof stick sample spread on a piece of glass showed what appeared to the operator as a sufficient quantity of grain for the purpose. This is achieved by the use of a hand microscope, but can be done without it if one's eyesight is good enough.

Further nucleation was usually stopped by lowering the vacuum and taking in a 'big drink', which means that the temperature was raised and the concentration decreased to the point where no new grain appeared. The trick now was to nurse these fine crystals so that their growth was rapid, without inducing the formation of additional ones.

Our observations show that for raw cane sugar syrup with purities of 82, boiled under 25" vacuum at sea level, the b.p. rise when nucleation starts is about 27° F (15° C). According to our tables, this corresponds to a supersaturation of around 1.75. Evidently, during the growing process the concentration had to be controlled to stay between 1.25 and 1.40 supersaturation, and herein lay the skill and experience of the sugar boilers, for they had only the vacuum gauge, the pan thermometer and proof stick to guide them, and thus had to depend on their sense of touch. If new grain appeared, the probability was that conglomeration occurred also. The false grain could be eliminated by feeding in water slowly until it disappeared, but conglomeration once formed can only be eliminated by completely dissolving the grain. For that reason most sugar is conglomerated.

There are a number of weak points to this system.

In the first place, the quantity of grain produced is dependent entirely on the experience and judgment of the operator, which is subject to considerable variation among individuals, and even in the same individual according to how he feels.

In the second place, due to the excessively high concentration, the formation of a certain number of conglomerates is inevitable, where all means available should be used to avoid them as undesirable in the final product, making affination at the refinery difficult, or necessitating additional washing if refined sugar is being made.

The third objection is that the system can be used successfully only on fairly high purities, and would not be practical on molasses crystallization at apparent purities of 70 or less.

Then, the material in the pan while being crystallized is held at excessively high concentrations for too long a period, involving the danger of inversion and glucose destruction.

Finally, the entire operation is dependent on the skill, experience and prejudices of the sugar boilers, and is not amenable to any simple form of easily followed instructions which it should be for best results.

The process can be helped materially by the use of supersaturation control instruments, which would permit certain standardization, but estimation of the proper amount of grain present would still depend upon the operator, with no means other than eyesight on a proof stick sample to make this critical determination.

(ii) *Shocking*

The first big improvement in grain establishment came with the introduction of 'shocking', which was originally used by ZITKOWSKY in the American beetsugar industry. The accepted procedure consists of drawing into the pan a small quantity of fine grain with the simultaneous admission of air shortly after the point of saturation is reached. This mixture of sugar and air causes the formation of nuclei much before they would appear by the first method.

Without instruments this point can be ascertained with sufficient accuracy by the sense of touch, depending upon the length of a thread drawn between the thumb and forefinger on a proof stick sample. As soon as an appreciable thread appears by this test, it is time to shock.

With instruments the supersaturation should be between 1.10 and 1.20. By the time full nucleation is attained, the supersaturation will probably have reached 1.50, which is materially lower than the 1.75 in the first case, and the occurrence of conglomerates will be much reduced.

It will still be necessary to judge when there is enough grain by sight, using a proof stick sample on a piece of glass, and further formation arrested just as in the first case, namely by lowering the vacuum and taking in a drink. Possibly the drink might be avoided. At all events, the supersaturation

must now revert to the working zone included between 1.25 and 1.40 as before.

This graining system is much better than the first, as the concentration attained is lower throughout, which means less conglomerates and less heat injury, giving an all-around better product. However, dependence is still vested in the humanly variable skill of the sugar boiler.

ii) *Seeding*

The third and by far the best method for grain establishment is by complete seeding, and the successful development and standardization of this system is credited in English speaking countries to E. C. GILLETT, Technical Director of the California and Hawaiian Sugar Refining Company of Stockton, California. In this case grain is not formed in the pan at all, since the supersaturation is never allowed to exceed the working zone whose upper limit is fixed at 1.40.

The first requirement is a good reliable set of instruments by the use of which the correct supersaturation is known at all times. The prerequisites of stability of operating conditions as prescribed at the beginning of this discussion are indispensable; otherwise the indications of the instruments will be unreliable.

The seed to be used is finely powdered sugar mingled with isopropyl alcohol in which it is totally insoluble, with enough alcohol to maintain good fluidity. This according to GILLETT consists of 1 lb. (454 g) of sugar per liter of alcohol. The amount of powder to be used per 1000 cu. ft. (283 hl) of massecuite depends upon the fineness of the powder and the size of the ultimate sugar crystals wanted. In the last analysis, this will have to be determined by trial and error, and is quickly standardized. As a first trial, 1 lb. (454 g) of powder per 1000 cu. ft. (283 hl) of massecuite could be used to produce sugar crystals of 0.35 mm. diameter, which is about standard for low grade crystallizer strikes, and also corresponds approximately to fine granulated sugar.

Whereas the grist of the sugar powder and the amount of seed to be used as recommended by GILLETT give excellent results, this must not be taken to mean that coarser seed in greater quantity is not ever to be used. Quite the contrary; in certain refinery operations, when it is required to produce coarse sugar such as standard granulated or similar large grain products, it is very advantageous to use coarse seed and more of it, because by this means the difficult period of developing the footing is made much shorter, less delicate, and more easily controlled. The additional trouble and expense of this operation are well repaid by the saving of both time and difficulties,

not to mention the possible increase of steam consumption resulting from having to feed water to hold down the supersaturation.

Sometimes as much as 5% of the weight of the sugar produced is used as seed. Thus, in a large pan producing 100,000 lb. (45,400 kg) of sugar per strike, 5,000 lb. (2,270 kg) of seed may be used. This involves a weight development of the crystals of 20 to 1, and consequently the size of the grain used for seeding must be proportional to the reciprocal of the cube root of 20, which is 0.37; and there would result the following.

For 0.5 mm sugar, use seed $0.37 \times 0.5 = 0.185$ mm

For 1 mm sugar, use seed $0.37 \times 1 = 0.37$ mm

For 2 mm sugar, use seed $0.37 \times 2 = 0.74$ mm

For 3 mm sugar, use seed $0.37 \times 3 = 1.11$ mm

For such an operation special preparations and equipment are required. A large hopper must be mounted to receive the seed, and from the bottom of this hopper to the pan must be an appropriate pipe, as direct and free from bends as possible, with gate valve. In this case, no alcohol is used.

For this seeding operation about ten minutes are needed, during which time steam must be shut off and vacuum held constant. After the seeding is completed, the control is the same as for fine powder seeding, outlined below.

The procedure is very simple. It is preferred for introduction of seed into the pan to have a seeding funnel just above the upper tube sheet, with a connection to the pan of not over 3/4" diameter, as short and direct as possible, and provided with a quick opening gate valve. Below is a thumb-nail summary of the instructions to the sugar boilers on the subject.

(1) Depending on the type of supersaturation instrument used, either attach a chart of the purity of the material to be crystallized, or make the proper adjustment for purity.

(2) Charge the pan, and during the formation of the nuclei, maintain the level above the upper tube sheet. Hold the vacuum at 4" to 5" (101.5 to 127 mm) absolute, and turn the steam on full.

(3) When a supersaturation of 1.25 is reached, seed the pan without allowing any air to enter for fear of provoking the formation of additional nuclei by shocking.

(4) As soon as the supersaturation approaches 1.40, lower the vacuum by 3" (76.0 mm).

(5) Remain inside the working zone defined as between supersaturations 1.25 and 1.40.

(6) After the footing is tightened, begin to feed normally without

loosening the massecuite and raise the vacuum *gradually and slowly* back to normal *in not less than 15 minutes*.

(7) If the pan is equipped with an automatic feeding system, it should be placed in operation as soon as the massecuite is tightened, as indicated by the wattmeter, whose contact should be set at 75% of the dropping power load when the strike is discharged.

(8) No further attention will now be required until the pan is full and ready for final concentration, when the wattmeter contact should be advanced a few kilowatts beyond the dropping load, so that if the sugar boiler is not present when the final reading is reached, the automatic will again start to feed, thus avoiding dangerous overloads. Immediately upon reaching the dropping load, stop the circulator.

(i) *Significant Observations on Pan Operation*

At this point it is deemed appropriate to make some observations based on extensive experience with the operation of vacuum pans which might shed interesting light on the problems involved.

(a) Uniformity of initial nuclei

Quite a point has been made in various writings about sugar crystallization regarding the necessity of obtaining the greatest possible uniformity in the size of the grains of powder to be used for seeding vacuum pans. Our experience has indicated that the importance of this feature has been exaggerated, and that extreme regularity is relatively unimportant, as can be gathered from the following simple facts. Consider the characteristics of any solid of regular form, such as sugar crystals, and observe that:

- (1) the linear dimension varies directly with the magnitude of the crystal;
- (2) the surface of the solid varies with the square of the linear dimension;
- (3) the volume and weight vary with the cube of the linear dimension.

Example

The dominant factor controlling the rate of growth of sugar crystals is the area of their surface exposed to the supersaturated solution-mother liquor, syrup or molasses. The weight of individual small grains in the powder when first introduced as seed into the pan is a very difficult matter to determine. They are microscopic in size.

A practical example might shed light on the subject. In a large sugar refinery 2 lb. of powder were used to seed a pan which produced 2000 cu. ft. (567 hl) of 'fillmass', from which was obtained about 100,000 lb.

(45,300 kg) of commercial fine granulated sugar. No new crystals were formed during the boiling operation, and hence the number of nuclei in the 2 lb. (0.9 kg) of powder was the same as the number of crystals in the 100,000 lb. (45,300 kg) of sugar, so that:

(a) the increase of weight and volume was $\frac{100000}{2} = 50000 : 1$,

(b) the increase in crystal surface was $1362 : 1$,

(c) the increase in linear dimension was $36.9 : 1$.

If, as was suggested, the diameter of the finished sugar crystals was 0.35 mm., then the grains of powder must have been of an average diameter of around 0.01 mm. The point of importance is that considerable variations of weight of the ultimate individual crystals involve relatively smaller variations of their linear dimension. Thus, it can be seen that single crystals weighing one-half as much as others would have their linear dimension reduced by only about 20%, a variation which to the eye is relatively unimportant, and substantially negligible from the standpoint of satisfactory commercial sugar.

(ii) *Small crystals grow faster*

Since the rate of increase of weight and volume is directly proportional to the surface of the crystals, it follows that the smaller crystals will gain weight and volume at a greater relative rate than the larger ones. In fact, the rate of weight and volume increment of the individual crystals per lb. of sugar will be inversely proportional to their size. This extremely important fact becomes an automatic corrector of irregularity. It is our inevitable conclusion that excessive size variations have been due not to irregularities of the size of the grains in the seed, but rather to the fact that during the strike new grains are formed at a time when they are neither wanted nor expected. All of this probably came from conditions prevailing in the pan, which were not suitable for the uniform growth and development of the crystals, and hence the defective result.

(iii) *Preparing the grain*

The method for the development of the grain was given in the operating instructions for the use of supersaturation control instruments. More details are required to have a complete understanding of what goes on and why.

After the introduction of the seed follows the development of the nuclei or seed grain to a visible size of approximately 0.05–0.10 mm linear. This

is called 'hardening the grain' by operators, and consists of preventing the formation of new nuclei while at the same time obtaining the maximum speed of growth in existing ones, until they are large enough to adsorb sucrose from the surrounding mother liquor as fast as it is made available by evaporation, which are easy words to say but of major significance. In the example of a refinery strike given above, it was pointed out that when the pan is seeded, the crystal surface for adsorption of sucrose is only 1:1362 of what it will be when the strike is finished, and hence a very critical condition exists in the inability of these crystals to adsorb sucrose as fast as it is made available by evaporation. In the instructions, two steps are taken to help out. First, as soon as the supersaturation approaches the danger line of 1.40, the vacuum is lowered from 5" absolute to 8" absolute, which increases the vapor temperature from 134° F (56.7° C) to 152° F (66.7° C). As a result of this the supersaturation now drops from 1.40 down to about 1.20 at a massecuite temperature of 168° F (75.6° C); and there will be no danger of nucleation until this massecuite temperature exceeds 171° F (77.2° C), so that a time of grace has been secured.

In addition, KUCHARENKO in his data has proven the fact that as the temperature increases, by such an amount, there is an increase in the speed of crystal growth several fold. If during the operation the supersaturation increases to the danger point, then the rate of evaporation can be reduced accordingly by lowering the steam pressure at the heating surface to correct this condition, being careful not to allow any variation of vacuum to take place. The other alternative would be to feed more syrup into the pan, and thus hold down the supersaturation. This is not advisable, however, because it increases the volume of the footing before it is brought together, making the ultimate problem more difficult. For that reason a drink before tightening the footing is not the best solution, unless the level is too low for circulation.

iv) *The critical point*

Gradually the crystals grow, and their capacity to adsorb sucrose from the surrounding supersaturated solution increases to the point where it equals and surpasses the ability to maintain the high supersaturation by the rate of evaporation in the pan, and here occurs a very interesting reaction, quite suddenly. It must be understood that immediately after seeding the volume of the crystals as compared to the volume of the footing is extremely small, and as they grow in size their volume increases more and more, and the volume of the mother liquor decreases accordingly due to evaporation. The critical point is reached when the volume of the void spaces between

the crystals is just about equal to the volume of the mother liquor, and that is the right point at which the strike should be carried for white liquor.

Several very surprising reactions take place suddenly upon reaching the critical point:

- (1) The boiling point rise suddenly drops by about 3°F . (1.66°C).

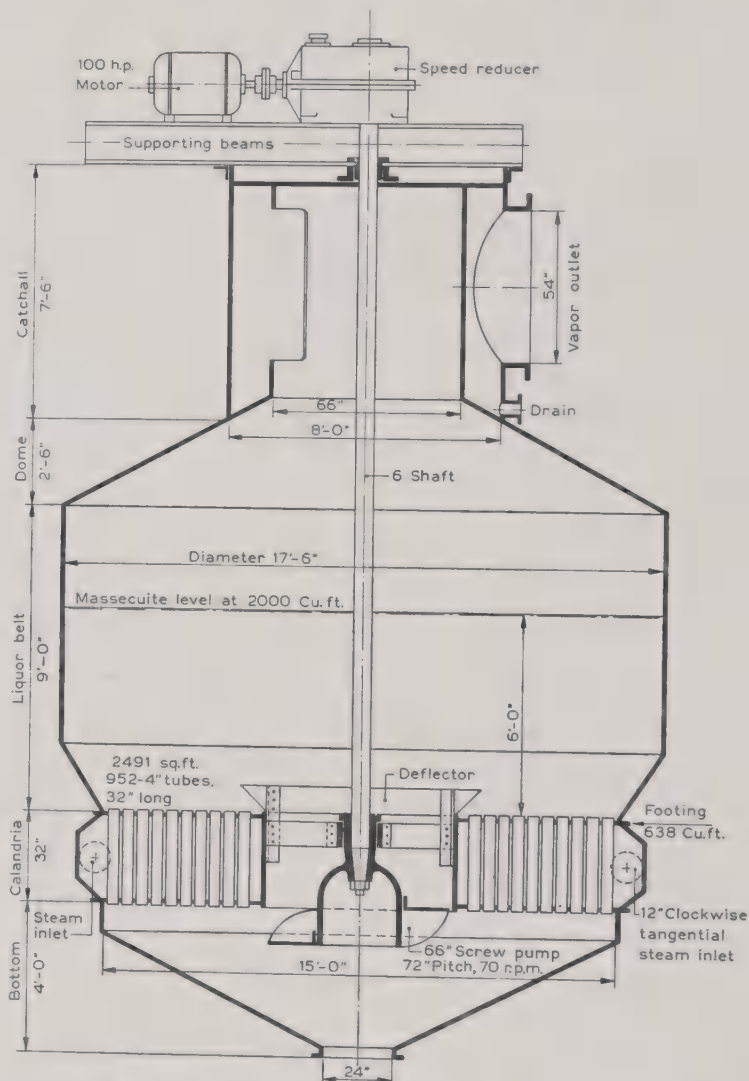


Fig. 11/23. 2000 cu. ft. low head calandria vacuum pan ($15' \times 17'6''$) equipped with mechanical circulation (Imperial Sugar Co., Sugarland, Texas).

- (2) The rate of evaporation increases greatly as has been actually observed on a flow meter indicating the steam consumption of the pan.

This situation requires immediate attention, as the rate of feed must now be increased to a maximum or the pan will freeze. With mechanical circulation and automatic feed, it is a very simple matter not only to face this

condition, but also to take advantage of it by adjusting the contact of the wattmeter so that the maximum is indicated on the steam flow meter. By this means a very considerable improvement has been made possible not only as regards capacity but also quality, because, when the massecuite is in this condition, the concentration of the mother liquor is considerably reduced, and the possibility of the occurrence of either false grain or conglomerates ceases.

An interesting fact is that one can leave the critical phase simply by over-heating and loosening the strike, after which it can be brought together again with the same original results. It is felt that the ordinary refinery sugar boiler always remains below the critical phase, and hence loses time and makes sugar of not as good quality as it can be made following the new technique.

After the critical phase is reached, the indications of supersaturation instruments have no significance of any value, and hence in our practice they are not used beyond this point.

This critical phase does not occur in making strikes of purities below 90. At least, it has never been observed during our experience, and in such cases, without mechanical circulators, supersaturation instruments can be used longer.

(j) *Vacuum Pan Tests*

A certain routine for testing vacuum pans has been established, and it was thought appropriate to present one of these tests for consideration here. The example selected is the performance of a 2000 cu. ft. refinery pan (Fig. 11/23) completely equipped as recommended herein making a white liquor strike, the log of which is given (Table 5).

(a) *Description of pan*

This pan represents a recent design and has the following characteristics.

(α) *Calandria*. The calandria is 15'0" (4.560 m) diameter and only 32" (0.813 m) high from out to out of tube sheets. It is provided with 952-4" (0.1015 m) No. 14 o.d. copper tubes, giving a total of 2491 sq. ft. (about 231 sq. m.) measured on the steam side. The downtake is 66" (1.680 m) diameter, and attached to the upper end is a funnel-shaped deflector at an angle of 45°, the top being 82" (2.080 m) diameter. There is provided an annular space in the shell of the calandria for the unobstructed admission of steam, 9" (228 mm) wide all around, without any baffles, ports or openings – in other words, wide open to the tubes. Steam is admitted tangentially through two 12" (0.305 m) inlets located 180° apart, both entering

TABLE 5

IMPERIAL SUGAR CO.
SUGAR LAND, TEXAS,
OCTOBER 9, 1954.

TEST OF 15'-0" × 17'-6" CALANDRIA VACUUM PAN
WITH 66" MECHANICAL CIRCULATOR
HEATING SURFACE, 2491 SQ. FT.

STRIKE: $\begin{cases} \text{CU. FT.} = 2000 \\ \text{PUR.} = 99.4 \\ \text{BRIX} = 89.4 \end{cases}$

Time of the observ.	Steam to pan		Indicated by control instrum.					Apparent supersat. b.p. rise	Automatic feed control			White liquor feed to pan			Masse-cuite		Steam and heat transmission				Remarks
	press. in lb.	temp. in °F	abs. in Hg	vapor temp. in °F	massec. temp. in °F	apparent temp. in °F	on		off	kW	brix	temp. in °F	pur.	st. gl.	ht. in.	lb./h	Steam consum. in lb./sq. ft./h	ΔT (steam-massec.)			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	
8:57	10.0	240																			
9:00	10.0	240	5.44	137.0	149.0	12.0	1.015		+	28.0	70.6	154	99.2			25,000	10.04	91.0	111.0	Steam on	
9:05	10.0	240	4.90	133.0	146.0	13.0	1.150		+	29.0	70.6	154	99.2	2.0	18.0	24,000	9.65	94.0	103.2		
9:10	10.0	240	4.90	133.0	148.5	15.5	1.350		+	29.0	70.6	154	99.2	2.0	18.0	29,000	11.67	91.5	128.2	Seed at 132.5 — 149.8=17.3 b.p. rise at 9:13	
9:15	10.0	240	4.90	133.0	151.5	18.5	1.575		+	29.0	70.6	154	99.2	2.0	18.0	24,000	9.65	88.5	109.7	Check to 8" abs. (133 — 151.5 — 18.5 b.pr.)	
9:20	10.0	240	7.76	151.0	168.0	17.0	1.295		+	?	70.6	154	99.2	2.0	18.0	16,000	6.44	78.0	90.0		
9:25	10.0	240	7.57	150.0	169.5	19.5	1.440	+		24.0	70.6	154	99.2	2.0	18.0	18,000	7.25	70.5	103.4		
9:30	10.0	240	7.20	148.0	163.5	15.5	1.120	+		24.0	70.6	154	99.2	2.5	24.5	33,000	13.25	76.5	174.4	Auto-feed on at 9:27	
9:35	10.0	240	7.76	151.0	171.0	20.0	1.480	+		24.0	70.6	154	99.2	2.5	24.5	35,000	14.04	69.0	205.0		
9:40	10.0	240	6.75	145.5	163.0	17.5	1.370	+		24.0	70.6	154	99.2	3.0	31.0	39,000	15.65	77.0	204.5		
9:45	10.0	240	6.51	144.0	161.5	17.5	1.385	+		24.0	70.6	154	99.2	3.0	31.0	38,000	15.25	78.5	195.4		
9:50	10.0	240	6.35	143.0	160.0	17.0	1.360	+		24.0	70.6	154	99.2	4.0	44.5	42,000	16.85	80.0	212.0		
9:55	10.0	240	6.03	141.0	159.0	18.0	1.450	+		24.0	70.6	154	99.2	5.0	59.0	43,000	17.25	81.0	214.0		
10:00	10.0	240	5.88	140.0	158.5	18.5	1.500	+		24.0	70.6	154	99.2	5.0	59.0	42,000	16.85	81.5	208.0		
10:05	10.0	240	5.73	139.0	157.5	18.5	1.505	+		24.0	70.6	154	99.2	5.0	59.0	42,000	16.85	82.5	205.5		
10:10	10.0	240	5.73	139.0	157.0	18.0	1.470	+		24.0	70.6	154	99.2	6.0	72.5	40,000	16.05	83.0	194.5	Feed closed	
10:15	10.0	240	5.44	137.0	156.0	19.0	1.565	+		40.0	70.6	154	99.2	6.0	72.5	38,000	15.25	84.0	182.5	steam off	
10:17	10.0	240								72.0											

Superheated steam used. Heat released per lb. = 1006.9 B.Th.U.'s

TABLE 5 (CONTINUED)

SECOND TEST

{ CU. FT. = 2000
 STRIKE: { PUR. = 99.4
 { BRIN = 89.2

Time of the observ.	Steam to pan		Indicated by control instrum.					Apparent supersat.	Automatic feed control		White liquor feed to pan		Masse-cuite		Steam and heat transmission					Remarks
	press. in lb.	temp. in °F	abs. in Hg	vapor temp. in °F	massec. temp. in °F	apparent temp. in °F	b.p. rise		on	off	kW	brix	temp. in °F	pur.	st. gl.	ht. in.	lb./h	Steam consum. in lb./sq. ft./h	Δ T (steam-masse.)	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
11:58	5.0	227																		Steam on
12:00	5.0	227	5.73	139.0	149.0	10.0	0.870		+	30.0	70.5	154	99.4	2.5	24.5	15,000	6.04	78.0	79.0	
12:05	5.0	227	4.71	131.5	144.0	12.5	1.131		+	30.0	70.5	154	99.4	2.5	24.5	17,000	6.83	83.0	83.8	
12:10	5.0	227	4.90	133.0	147.0	14.0	1.235		+	30.0	70.5	154	99.4	2.5	24.5	22,000	8.85	80.0	112.8	
12:15	5.0	227	4.90	133.0	148.5	15.5	1.344		+	30.0	70.5	154	99.4	2.0	18.0	22,000	8.85	78.5	115.0	Seed at 132.5 — 149.0 = 16.5 b.p. rise
12:20	5.0	227	4.90	133.0	150.5	17.5	1.500		+	30.0	70.5	154	99.4	2.0	18.0	18,000	7.25	76.5	96.6	Check to 8" abs. (132.5 — 151.0 = 18.5 b.p. rise)
12:30	5.0	227	7.57	150.0	167.5	17.5	1.330	+		30.0	70.5	154	99.4	2.0	18.0	16,000	6.44	59.5	110.2	
12:45	5.0	227	7.57	150.0	169.0	19.0	1.425	+		24.0	70.5	154	99.4	2.5	24.5	32,000	12.85	58.0	226.0	
1:00	5.0	227	6.43	143.5	161.0	17.5	1.390	+		22.0	70.5	154	99.4	4.0	44.5	36,000	14.45	66.0	223.5	
1:15	5.0	227	5.16	136.0	156.5	20.5	1.635	+		28.0	70.5	154	99.4	5.0	59.0	33,000	13.25	70.5	191.8	
1:30	5.0	227	5.16	136.0	155.5	19.5	1.610	+		33.0	70.5	154	99.4	6.0	72.5	28,000	11.23	71.5	160.0	
1:35	5.0	227	5.16	136.0	155.0	19.0	1.575	+		70.0	70.5	154	99.4	7.0	86.5	28,000	11.23	72.0	159.0	Total steam used, 42,300
11:36	5.0	227														23,000	8.88			

Superheated steam used. Heat released per lb. = 1020 B.Th.U.'s.

Superheated steam used. Heat released per lb. = 1020 B.Th.U.'s.

in a clockwise direction, and provides free and maximum flow of steam through the annular space and completely fills it, giving equally distributed heat to all parts of the heating surface. Non-condensable gases and condensate are removed from the centre at the lower tube sheet.

(β) *Bottom*. The bottom is conical at an angle of 20° with the horizontal, and has a 12" (305 mm) cylindrical section between the conical part and the calandria. The discharge valve is 24" (610 mm) diameter, and has openings for cut over, feed and washout.

(γ) *Liquor Belt*. The liquor belt, just above the calandria, is 17'6" (5.340 m) diameter and is attached to the calandria by a conical reducing section having an angle of 30° with the vertical. The height of the liquor belt is about 9'0" (2.75 m), leaving a free unoccupied height of 3' (0.915 m) above the maximum massecuite level at rated capacity of 2000 cu. ft. (566 hl), which is 6 ft. (1.825 m) above the upper tube sheet. This belt makes the pan of the low head type now in general use.

(δ) *Dome and Catchall*. Above the liquor belt is the usual dome, reducing the diameter from its original to about 8'0" (2.44 m), where a catchall of this size is attached, having a 54" vapor outlet (1.375 m) connecting to the condenser, which is of the SCHUTTE & KOERTING M.J.S. design of ample capacity.

(ii) *Equipment*

This pan has the following equipment, which is very complete in all respects.

(1) One (1) 66" (1.680 m) mechanical circulator having 72" (1.830 m) pitch, driven by a 100 h.p. motor, and turning at 70 r.p.m., giving a displacement of 7930 cu. ft. (2240 hl)/min. The volume of the strike produced by the pan is 2000 cu. ft. (567 hl) so that when the pan is full, its entire contents are turned over by the circulator 3.96 times per minute. Another interesting fact is that since the inside area of the tubes is 76.5 sq. ft., the velocity in the tubes is the ratio of the displacement of the circulator to this area, and this is 132.0 cu. ft./sec, which gives a speed of 1.73 ft. (527 mm)/sec, a figure considerably above the standard of 1.50 (457 mm) suggested previously.

(2) Automatic feeding system, consisting of a 6" (153 mm) air operated diaphragm valve actuated by a contacting adjustable wattmeter attached to the driving motor circuit, which can be set to any motor load. There is also an adjustable electric-pneumatic time delay relay interposed between the wattmeter and the diaphragm valve, by means of which the lengths of the drinks can be adjusted, since the feeding is not continuous. Hand feeding is also provided on a by-pass connection, which has to be used at

the beginning for charging the pan, and in case of repairs or emergency.

(3) A set of supersaturation control instruments with charts for all purities within the desired range giving the boiling point rise as well as the vapor temperature and the massecuite temperature in the centre of the downtake.

(4) A MINNEAPOLIS HONEYWELL automatic vacuum control, operating on the water supply and capable of adjustment to any vacuum within the usual operating range, and holding it accurately well within the tolerance of 0.1" of mercury (2.54 mm).

(5) A MINNEAPOLIS HONEYWELL steam pressure regulator of capacity sufficient for the pan, reducing the pressure from the 40 lb. line to whatever is required at the calandria.

Besides this unusual equipment, the ordinary accessories are provided, including an attachment for seeding the pan with powdered sugar and isopropyl alcohol. Also, there is a large seeding hopper with connections to the pan by which any amount of seed can be drawn in as needed, which serves very well for the production of large grain sugar crystals such as standard granulated or specials.

ii) *Comments on the design*

This pan is of the 'low head' type, which favors good performance for all kinds of sugar crystals and eliminates excessive undesirable temperatures, all of which has been fully discussed previously.

The most remarkable feature is the small amount of heating surface in proportion to the capacity of the pan, only 2491 sq. ft. for 2000 cu. ft. of strike capacity, which is a ratio of only 1.245. Nevertheless, the time required to make a strike compares very favorably with that of pans with ratios of 1.75 or more, which confirms GILLETT's and also others' often expressed opinion that after the tubes reach a length of 3 ft., it is a waste of material to make them longer.

The height of the massecuite above the upper tube sheet at the rated capacity is 6 ft. (1.83 m). With the circulator in operation, this might very well be increased to 8 ft. (2.430 m) with little reduction of the rate of evaporation, thus gaining another 500 cu. ft., boosting the strike volume to 2500 cu. ft. (708 hl). The tests show that the final reading taken when the strike was about to be dropped was only slightly below the recorded maximum rate of steam consumption, which is characteristic of mechanical circulation.

Another relatively new feature of the pan is the fact that the entire unit with the exception of the tubes is nickel clad, even including the tube sheets.

This has resulted in the total absence of iron oxide particles, which has eliminated the presence of black specks in the white sugar usually found in the first strikes made after a shut-down.

(iv) *Performance*

The log of the two tests reported accompanies (Table 5), but only the one where 10 lb. pressure was used will be analysed, since it fairly represents normal field performance. Actually, the pan has also been operated with 15 lb. steam pressure, and the duration of the 2000 cu. ft. strikes for these various conditions was as follows, with the feed at the same brix, slightly above 70:

Time required for 15 lb. steam 1 : 08

Time required for 10 lb. steam 1 : 20

Time required for 5 lb. steam 1 : 38

Column 1. This column gives the time of the observations every five minutes.

Column 2. The steam was always exactly at 10 lb. pressure, controlled by the automatic regulator drawing from the 40 lb. line superheated, and hence each pound condensed in the pan gave up more than the theoretical latent heat at that pressure. This was determined at 1006.9 B.Th.U.'s/lb.

Column 3. The steam temperature shown here is the saturation temperature prevalent in the heating surface because the rapid condensation at the tubes will absorb all the superheat, and for all practical purposes the temperature inside the calandria will correspond to that at saturation.

Column 4. The absolute pressure in inches of mercury was read from the absolute pressure gauge forming part of the supersaturation control instruments. The vacuum, if that is desired, can be obtained by subtracting the observed absolute pressure from the barometer as read at the site of the factory. It will be understood that the absolute pressure does not vary with the elevation, but the vacuum would, so that these observations would have the same significance no matter where the plant is located.

Column 5. The vapor temperature was read on the temperature scale of the absolute pressure manometer, and is correct.

Column 6. The massecuite temperature was read on the 12" mercury dial thermometer, which had previously been very carefully calibrated against the absolute pressure gauge while boiling water under vacuum in the pan slowly, and at a low level. The sensitive element of this thermometer was located in the centre of the downtake, where it can reasonably be expected to give temperatures not much affected by the hydrostatic head.

Column 7. The boiling point rise is obtained by subtracting the vapor temperature from the massecuite temperature, noted as 'apparent b.p.rise'. The reason for this is that the massecuite thermometer does read high, due presumably to shortcircuiting massecuite into the downtake without flashing completely to vacuum equilibrium. This is probably due to the tremendous draft of the circulator not satisfied with the cooled material

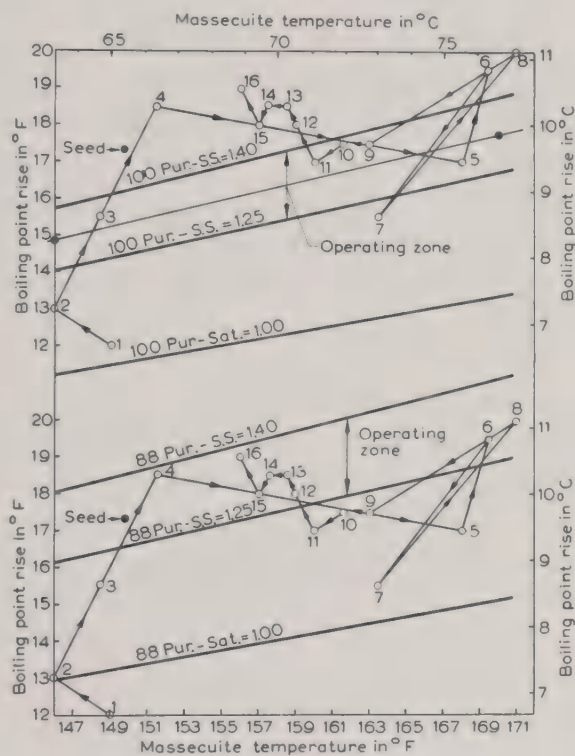


Fig. 11/24. Graph showing supersaturation for pan test using 100 and 88 purity charts.

coming to it from the boiling surface. This was the reason for installing the deflector at the downtake.

Column 8. The above situation threw off the indications of supersaturation to such an extent that it was necessary to compensate by the use of an 88 purity chart on the instruments instead of the indicated 100 corresponding to the purity of the white liquor of 99.2. With the normal 100 purity chart, when the pan was seeded by its indications, the powder vanished completely as if the pan had not been seeded, and successful seeding was effected only after lowering the purity of the chart to 88.

The supersaturation shown in this column was derived from the actual observations of vapor and massecuite temperature referred to the 100 purity

chart. There is submitted herewith a graph (Fig. 11/24) in which both the conditions indicated by the 100 purity chart and the 88 purity chart are plotted showing the saturation line and the operating zone included between supersaturations of 1.25 and 1.40. The points for all observations taken during the test are plotted in both cases, and numbered in the order in which they were made. The seeding point is also shown.

If the seeding had been done according to the 100 purity chart at a masse-cuite temperature of 150, the indicated supersaturation would have been 1.25, and the b.p. rise 14.5. If these two are now plotted on the 88 purity chart, the supersaturation becomes 1.09, and this concentration is not enough to prevent the fine nuclei from dissolving when they pass through the tubes, and hence they disappear.

On the other hand, the fourth reading of the test was made at a masse-cuite temperature of 151.5 with a b.p. rise of 18.5. With the 88 purity chart, this gives a supersaturation of 1.38, which is within the limits of the working zone of 1.40. However, if these same readings are now referred to a 100 purity chart, the supersaturation becomes 1.58, at which there would surely result the formation of additional grain, 'smear', but no false grain were formed, and hence the situation is normal.

At the temperature limits of 146° F and 170° F at which the graph is drawn, we have the following.

B.p. rise at		88 Chart	100 Chart	Diff.
146° F	at sat.	12.9	11.2	1.7
146° F	at 1.25	16.1	14.0	2.1
146° F	at 1.40	18.1	15.7	2.4
170° F	at sat.	15.1	13.4	1.7
170° F	at 1.25	18.9	16.7	2.2
170° F	at 1.40	21.2	18.8	2.4

The curves are all straight lines, and hence easy to plot with only two points.

About the plot of the pan performance points on the graph, the first three represent the work of concentration before grain establishment. Seeding was done at the black circle indicated, and at point 4 the vacuum was dropped from 4.90" abs. to 7.27 abs., which raised the temperature of the masse-cuite, and lowered the supersaturation to considerably below 1.25, after which it rose again to within the working zone. Between readings 6 and 7 there occurred the 'critical point' which brought the b.p. rise down

to 15.5 at the same time greatly increasing the rate of evaporation to almost twice what it was just before. As a result, the automatic vacuum control was not quick enough and reading 8 brought an abnormally high temperature, which was quickly corrected by reading 9. After this the subsequent readings gradually reverted to normal, and from 9 to 16 remained within the working zone, or close to it.

After the automatic feed is on, reading 6, since the feed is by drinks and not continuously, there result oscillations of concentration, becoming lighter when the feed valve is closed and lighter when it is open. Not only that, but the operator was in the gradual process of raising the vacuum slowly, as can be seen, and each time it was raised a little this was accompanied by a gush of evaporation which also had something to do with the irregularities noted.

Column 9 and 10. These columns simply indicate when the automatic feed was on and when it was off.

Column 11. This column gives the electric load on the motor driving the circulator. There is nothing remarkable about this, except to note the sudden and enormous change which takes place very quickly after the feed to the pan is closed off for final concentration. In the short space of two minutes the load was almost doubled, and this indicates the necessity of being vigilant at this stage, and to raise the point of contact of the wattmeter only slightly beyond the expected end-point; otherwise, if the operator is absent, serious overload may occur with danger of damage to the motor, and particularly to the speed reducing gear.

Column 12, 13 and 14. These three columns give the brix, temperature and purity of the white liquor fed to the pan, and were all constant during the test.

Column 17. This column gives the steam consumption of the pan in lb./h at each observation. These data were plotted on a separate graph, and show that the rate of evaporation towards the end of these refinery strikes was almost double what it was before grain establishment, which in general is very different from what it would be on a raw strike, particularly a low grade (Fig. 11/25).

These readings were made on the steam flow meter, and the automatic feed after it was turned on was adjusted to produce maximum steam flow, which was initiated at 9 h 25'. It is a very mistaken idea to think that maximum steam flow occurs while the strike is loose. If the massecuite is loosened after being brought together, then everything reverts to the same condition before tightening; namely, the steam flow decreases, the boiling point rises, and it becomes necessary to start all over again or else lose much time.

Attention is again called to the very short lapse of time (2 min) from when the feed was shut off until final concentration of 89.4 brix was attained.

The steam flow reading was at the rate of 38,000 lb./h, and for the two minutes between this reading and the shutting off of steam, the amount of evaporation was 1,270 lb. If this amount of water is added to the strike which was dropped at 89.4 brix, this brings the concentration during the main part of the operation to 88.7 brix, which is very tight indeed, and is well worth remembering.

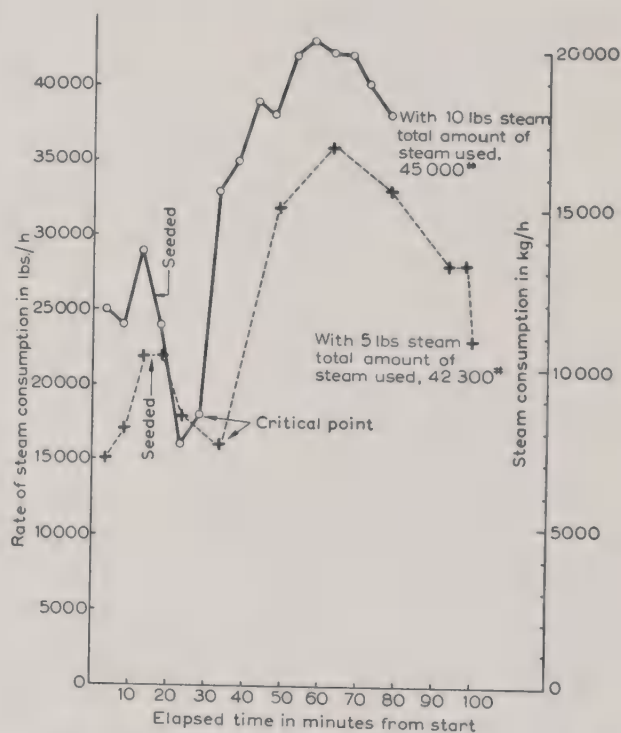


Fig. 11/25. Rates of steam consumption on 2000 cu. ft. refinery skip, using 5 lb. and 10 lb. steam pressures. (Imperial Sugar Co., Sugar Land, Texas, 1954).

Column 18. This column gives the rate of steam consumption used in lb./sq. ft./h, and parallels the over-all steam consumption. The peak here is 17.25, and the minimum 6.44, the end-point being 15.25. This column is an intermediate step in the determination of the heat transmission given below.

Column 19. The ΔT or the difference between steam on one side of the tubes and massecuite on the other, is given here. It was obtained by subtracting the temperature of the massecuite as observed from the saturation temperature of steam also given in the log. The questionable point is what is the average temperature of the massecuite as it passes through the

tubes. The procedure given here indicates the temperature at the entrance of the tubes below. The boiling point as massecuite leaves the tubes is not known, but it would certainly be greater. How much greater would depend upon the amount of evaporation taking place in the tubes, and this is variable according to the effect of the hydrostatic head. A mere guess would indicate as follows:

(a) the cu.ft./min moved by the circulator is estimated at 7930. At 9.4 brix, this weighs 726,000 lb. The specific heat of massecuite taken at 525. Steam used per minute: average 562 lb. B.Th.U.'s released, $562 \times 1006.9 = 566000$. Increase in massec. temp. 1.485.

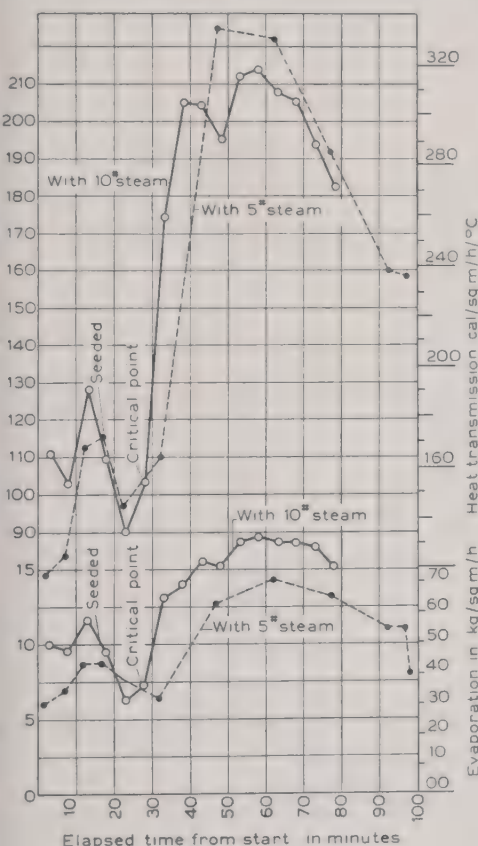


Fig. 11/26. Heat transmission and steam consumption during the making of a fine granulated skip with 5 lb. and 10 lb. steam pressures (Imperial Sugar Co., Sugar Land, Texas, 1954).

aneously, and were found to be almost identical when steam at saturation was used. In this case, the amount of heat released per lb. of steam condensed was 1006.9 B.Th.U.'s, whereas at saturation it is 952.2, an increase of 5.7%.

(b) Inasmuch as the average ΔT is around 90, this correction might increase the calculated heat transmission by perhaps 2%, which is not significant.

Column 20. The heat transmission (Fig. 11/26) was obtained by multiplying the amount of evaporation sq. ft./h by the heat released by condensing 1 lb. of steam, given here as 1006.9, and dividing by the ΔT . The average value of this for the entire test is 154, which is the highest this writer has ever recorded by a substantial margin, many pans not reaching 100.

(v) *Comments on results of test*

The amount of evaporation involved in the making of the strike is not given in the log. In other tests where facilities were available, both steam consumption and evaporation were determined at each observation simul-

Note the following:

Brix of strike	89.4	
Solids per cu. ft.	82.054	lb.
Solids for 2000 cu. ft.	164,108	lb.
Weight at 70.6 brix (density of feed)	232,500	lb.
Weight at 89.4 brix (density of strike)	184,000	lb.
Evaporation	48,500	lb.
Steam used (by meter reading)	45,000	lb.
Steam used, corrected for superheat	47,600	lb.
Excess of evaporation over saturated steam	900	lb.
Which is only the negligible amount of	1.9%	

It is known that there is a certain amount of heat released by sucrose upon crystallizing, but as has been confirmed, it is not of significant magnitude, and the error involved in omitting the correction is neglected according to our practice.

It is felt that this pan gives an excellent performance as regards capacity, facility of control and operation. The use of the indicating, recording and integrating steam flow meter contributed considerably to the good results, and is now recommended as a valuable new accessory.

Aside from the deviation of the supersaturation control instruments, for which allowance was made, there were no operating difficulties. It was not necessary to take in big drinks, nor was movement water used at any time.

The most remarkable development was the high heat transmission well maintained after the 'critical point', averaging about 200% of what it was during the first six observations. Actually the value of U for this period was 107.6 B.Th.U.'s/sq.ft./h/degree difference between steam and massecuite, against 199.6 for the last ten, the very last being 182.5, and the general average, 154. The rate of evaporation parallels these figures.

Another surprising fact is that it took only two minutes to attain final concentration, and that the kW used by the driving motor on the circulator during that time rose from 40 to 72.

4. Application of Mechanical Circulators in the Sugar Industry around the World

The application of mechanical circulators has found its greatest introduction in the western hemisphere and furthermore in Australia. A number of sugar

roducing countries have not yet introduced mechanical circulation as additional improvement to increase the efficiency of pan operations.

In July 1956 the following number of mechanical circulators was installed in different countries:

<i>America</i>	
U.S.A. mainland	56 (12 beet, 42 refineries, 2 cane)
Hawaii	5
Puerto Rico	22
Canada	1
Cuba	32
Dominican Republic	3
Mexico	16
Panama	1
Venezuela	2
Ecuador	6
<i>Australia</i>	21
<i>Europe</i>	
United Kingdom	1
<i>Asia</i>	
India	5

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CHAPTER 12

CRYSTALLIZATION OF MASSECUITES BY COOLING

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1. Introduction

In sugar factories the main crystallization of sucrose takes place in the vacuum pans. For low purity boilings, in which the speed of crystallization is low, the exhaustion of the mother liquor cannot be pushed to the practical possible limit during the time available for the boiling process. For massecuites giving final molasses it is an absolute requirement, and for the other massecuites it is sometimes desirable and advantageous to continue the crystallization process which was interrupted at the end of the boiling process.

After leaving the vacuum pan the massecuites are stored in vessels properly called crystallizers. They are equipped with a slow revolving stirring gear and crystallization in motion takes place when the massecuite cools down gradually. The solubility of sucrose in the mother-liquor will be reduced as the temperature decreases. A part of the dissolved sucrose will be in a supersaturated solution and under proper conditions of temperature and mixing be deposited on the crystals already existing. The mother liquor will be more exhausted and the crystal yield will be increased.

When a massecuite is left to itself to cool off only by heat transfer to the surrounding atmosphere a considerable time is required to reduce the temperature from 70° to 40° C. In many sugar factories the crystallizers are not always placed in an ideal arrangement with a view to maximum heat exchange per unit of time. Therefore when no forced cooling via special heat exchange elements is applied a considerable number of crystallizers is required, occupying a large floor space, while investment and maintenance will be correspondingly higher.

It is understandable that many attempts have been made to invent and construct cooling systems by which the cooling time can be reduced. These cooling systems have been applied in sugar factories mostly for the forced

cooling of massecuites giving final molasses. The crystallizers in which the higher purity boilings are discharged are in many cases no more than strike receivers or storage tanks with a mixing device for the massecuite on its way from vacuum pans to centrifugals. Practically no cooling takes place during the short time of storage; therefore after-crystallization can be neglected.

In order to understand the applicable methods in treating a massecuite during the cooling period it is important to know the laws governing the crystallization of sucrose from impure sugar solutions. Our present knowledge of these laws is still imperfect. Even where there is justification in applying the available knowledge of crystallization the treatment of massecuites in crystallizers is still more or less subject to empirical considerations and is based on the practical experience and traditional methods of the technologist in charge of operations. Especially for afterproduct boilings, opinions among technologists as to cooling times and ways of treatment of massecuites in crystallizers differ widely. Recommended cooling times for a proper and efficient exhaustion of molasses vary from 90 to 10 hours or less. There is no general agreement as to the treatment of the massecuite during and after the cooling process.

To get the best results in the crystallizer station it is essential that the material, being the massecuite as discharged from the pan, enters the crystallizers in the most favorable condition for crystallization by cooling. For this purpose due attention has to be paid to the preceding stages of the fabrication process, especially the juice purification and the boiling process. The centrifugal station also must be dimensioned and equipped to give maximal results as to the separation of crystals and mother liquor (molasses).

2. Solubility of Sucrose in Pure and Impure Solutions

An essential value, which gives insight into the behavior of a sugar solution subject to crystallization, is the *degree of supersaturation*. It is expressed as the ratio

$$\frac{\text{sucrose \% water in the given solution of purity } P \text{ at } t^{\circ} \text{ C}}{\text{sucrose \% water in saturated solution of the same purity } P \text{ at } t^{\circ} \text{ C}}$$

The solubility of sucrose in impure solutions as compared to the solubility of sucrose in pure aqueous solutions is expressed by the ratio

$$\frac{\text{sucrose \% water in saturated impure solution at } t^{\circ} \text{ C}}{\text{sucrose \% water in saturated pure solution at } t^{\circ} \text{ C}}$$

known as the *saturation coefficient*.

The solubility of sucrose in saturated pure solutions has been determined by many investigators. Best known in the sugar literature is HERZFELD's solubility table, which by later investigators was reported not to be quite correct, especially for temperatures exceeding 60° C (see Vol. I, p. 21, section 4a).

TABLE 1
SATURATION COEFFICIENTS OF BEETSUGAR SOLUTIONS

Apparent Purity	Saturation coefficients				
	40° C	50° C	60° C	70° C	80° C
100	1.00	1.00	1.00	1.00	1.00
95	0.98	0.98	0.98	0.98	0.98
90	0.97	0.97	0.97	0.97	0.98
85	0.97	0.97	0.97	0.97	0.98
80	0.98	0.98	0.98	0.99	1.01
75	1.00	1.01	1.02	1.03	1.07
70	1.04	1.06	1.08	1.09	1.18
65	1.08	1.13	1.16	1.21	—
60	1.13	1.20	1.26	1.38	—

It has long been known that most inorganic salts tend to increase the solubility of sucrose while reducing sugars decrease the solubility. A marked difference will be, therefore, between the saturation coefficients of cane- and beetsugar solutions because the latter contain almost no reducing sugars in comparison with technical canesugar solutions.

Table 1 shows the saturation coefficients for beetsugar solutions at different temperatures and purities as determined by GRUT¹. The figures show that when the concentration of inorganic salts increases with decreasing purity the solubility of sucrose increases, especially at the higher temperatures. In the higher purity range the solubility of sucrose decreases at lower salt concentrations.

TABLE 2
SUCROSE % WATER IN SATURATED SOLUTIONS ($t = 40^{\circ}$ C)

Real purity	FRADISS	URBAN	SCHNELL and GEESE	HÖGLUND	BROWN, SHARP and DAHLBERG	BROWN and NEES	GRUT
100	2.38	2.38	2.38	2.38	2.38	2.38	2.38
95	2.39	2.42	2.32	2.30	2.32	2.30	2.33
90	2.45	2.47	2.30	2.24	2.29	2.26	2.30
85	2.53	2.52	2.32	2.20	2.29	2.25	2.30
80	2.64	2.59	2.35	2.19	2.31	2.27	2.32
75	2.75	2.66	2.40	2.24	2.35	2.32	2.38
70	2.89	2.75	2.48	2.36	2.41	2.42	2.48
65	3.02	2.87	2.63	2.53	2.62	2.60	2.58
60	3.15	3.02	3.00	2.77	—	3.05	2.70

Many research workers have felt the need for reliable solubility figures in saturated impure solutions in order to be able to determine the supersaturation of a given solution.

GRUT¹ reviews the result of their determinations in beetsugar molasses and reports his own determinations with Danish beetsugar products which are shown in Table 2 for a temperature of 40° C.

This table demonstrates considerable differences between the determinations of different investigators. GRUT's figures cannot be compared directly with the data of other sugar chemists since his figures are given for apparent purities.

When *calculating* the *supersaturation* of a solution with 75.0 purity and 80.0 dry substance having a sucrose/water ratio of 3.00, the following values will be found depending on the solubility table which is used:

FRADISS	1.09
URBAN	1.13
SCHNELL and GEESE	1.25
HÖGLUND	1.34
BROWN, SHARP and DAHLBERG	1.28
BROWN and NEES	1.29
GRUT	1.21

As the nature and the composition of the nonsugars influencing the solubility of sucrose are variable, generally acceptable solubility figures can never be given. Every sugar factory or sugar producing area, if we wish to know the solubility of sucrose in its sugar house products, has to determine from time to time the solubility values with its own material. But this can only be recommended where a sugar country or a sugar company, having a number of factories, has its own research organisation for this kind of investigations. This kind of study requires skill in experimental chemistry of the investigator, suitable laboratory equipment, and time.

For practical purposes the absolute value of the solubility figures is fortunately not of prime importance for technical control of the crystallization process as long as always the same solubility tables are used. The calculated supersaturations can be compared in this way. The absolute values of the supersaturation are not certain at all.

Table 3 gives a solubility table based on GRUT's figures². They have been determined in beet molasses of Danish origin. MCGINNIS³ reports that the figures have been found valid, on the average, for American beet molasses, although individual deviations may be great in the low purity materials.

This fact has also been observed by GRUT⁴, who now prefers to use the

TABLE 3
SOLUBILITY TABLE OF BEETSUGAR AT DIFFERENT APPARENT PURITIES AND DIFFERENT
TEMPERATURES (BASED ON THE FIGURES OF E. W. GRUT)
purities

Temp in °C	100	98	96	94	92	90	88	86	84	82	80	78	76	74	72	70	68	66	64	62	60	Temp in °C
30	218	216	215	214	213	212	212	212	212	213	214	215	217	218	220	221	223	225	227	229	231	30
32	222	220	218	217	216	215	215	215	215	216	217	219	220	222	224	226	228	230	233	235	239	32
34	226	224	222	221	220	219	219	219	219	220	221	222	224	226	228	231	234	237	240	243	247	34
36	230	228	226	225	224	223	222	223	223	223	224	226	228	230	233	237	240	243	247	250	254	36
38	234	232	230	228	227	226	226	226	226	227	228	230	232	235	238	242	246	250	254	258	262	38
40	238	236	234	232	231	230	230	230	230	231	232	234	237	240	244	248	252	256	261	265	270	40
42	243	240	238	236	235	234	234	234	234	235	237	238	241	245	249	253	258	263	268	273	279	42
44	248	244	242	240	239	238	238	238	239	240	241	243	246	250	254	259	264	269	275	281	288	44
46	252	249	247	246	245	244	243	243	244	245	247	249	252	256	260	265	270	276	283	290	297	46
48	257	254	252	251	250	249	248	248	249	250	252	255	258	261	266	271	277	284	291	298	305	48
50	262	260	258	256	255	254	253	253	254	256	258	260	263	268	273	278	285	292	299	306	314	50
52	268	265	263	262	261	260	259	259	260	261	263	266	269	274	279	285	292	299	307	315	324	52
54	274	271	269	268	267	266	265	265	266	267	269	272	276	281	286	293	300	308	316	325	334	54
56	280	277	276	274	273	272	271	271	272	273	276	279	282	287	293	300	308	316	325	335	345	56
58	286	284	282	280	279	278	277	277	278	279	282	285	289	294	300	308	317	326	336	346	357	58
60	293	290	288	286	285	284	284	283	284	285	288	292	296	301	308	316	325	335	346	357	370	60
62	300	297	295	293	292	291	291	290	291	293	296	299	303	308	315	324	324	344	357	370	385	62
64	307	305	303	301	299	298	298	297	298	300	303	306	310	316	323	333	343	355	369	385	401	64
66	315	313	311	309	307	306	306	305	306	308	311	314	319	325	332	342	352	366	381	399	418	66
68	323	321	319	317	315	314	314	314	315	316	319	323	328	334	341	351	363	378	395	415	437	68
70	331	329	327	325	323	322	322	322	323	325	327	331	337	343	352	362	375	391	410	432	457	70
72	339	337	335	333	332	331	330	331	332	334	337	342	349	356	364	376	390	408	429	454	481	72
74	349	347	345	343	341	340	340	340	341	343	347	353	361	369	379	392	409	430	457	487		74
76	358	356	354	352	351	350	350	350	351	354	358	365	373	383	395	409	431	458	490			76
78	369	367	364	363	361	361	360	361	362	365	370	377	387	398	412	429						78
80	380	377	375	374	373	372	372	373	374	378	383	392	402	415	430	450						80

ratio nonsugar/water instead of supersaturation as a guide for low grade crystallizer work.

The solubility determinations of sucrose in solutions containing cane juice impurities have not been as many as for beetsugar solutions. Best known are the investigations carried out by VAN DER LINDEN⁵ in Java

and JACKSON and SILSBEE⁶ in the U.S.A. at the National Bureau of Standards. These research men determined the solubility of sucrose in the presence of invert sugar. The figures show that invert sugar tends to decrease the solubility of sucrose.

The saturation coefficients as shown in Table 4 have been calculated by THIEME⁷, using the solubility figures found by JACKSON and SILSBEE.

TABLE 4
SATURATION COEFFICIENTS OF SUCROSE-INVERTSUGAR MIXTURES

Purity	30° C		Purity	50° C	
	Sucrose/ water	Saturation coefficient		Sucrose/ water	Saturation coefficient
79.0	196.0	0.89	84.6	243.7	0.94
70.0	187.6	0.86	70.4	228.4	0.88
62.3	180.9	0.83	58.8	215.1	0.83
51.1	168.4	0.77	43.7	196.4	0.75
40.5	153.3	0.70	33.1	190.8	0.73
31.6	147.9	0.68			
24.2	137.8	0.63			

The purities have been calculated as the ratio sucrose/sucrose + invert sugar. The influence of inorganic nonsugars on the solubility of sucrose has not been taken into account.

TABLE 5
SOLUBILITY TABLE OF CANESUGAR AT DIFFERENT REAL PURITIES AND DIFFERENT TEMPER.

Temp. in °C	purities																	
	100	98	96	94	92	90	88	86	84	82	80	78	76	74	72	70	68	66
26	211	209	207	205	203	201	199	197	196	194	192	190	188	186	184	182	180	178
28	215	213	211	209	207	205	203	201	199	197	195	193	191	188	186	184	182	180
30	218	216	214	212	210	208	206	204	202	200	198	195	193	191	189	187	185	183
32	222	220	218	216	214	212	210	207	205	203	201	199	197	195	193	191	189	187
34	226	224	222	220	218	215	213	211	209	207	205	203	201	198	196	194	192	190
36	230	228	226	224	222	219	217	215	213	211	209	207	204	202	200	198	196	194
38	234	232	230	227	225	223	221	219	217	215	212	210	208	206	204	202	199	197
40	238	236	234	231	229	227	225	223	221	218	216	214	212	210	207	205	203	201
42	243	240	238	235	233	231	229	227	224	222	220	218	216	213	211	209	207	205
44	248	244	242	240	238	236	233	231	229	227	225	222	220	218	216	214	211	209
46	252	249	247	245	243	240	238	236	234	231	229	227	225	223	220	218	216	214
48	257	254	252	250	247	245	243	241	238	236	234	232	229	227	225	222	220	218
50	262	260	258	255	253	251	248	246	244	241	239	237	234	232	230	227	225	223
52	268	266	263	261	258	256	254	251	249	247	244	242	239	237	235	232	230	227
54	274	271	269	266	264	262	259	257	254	252	249	247	244	242	239	237	234	232
56	280	277	275	272	270	267	265	262	259	257	254	252	249	247	244	241	239	236
58	286	283	281	278	275	273	270	267	265	262	259	257	254	251	249	246	244	241
60	293	290	287	284	282	279	276	273	270	268	265	262	259	257	254	251	248	246
62	300	297	294	291	288	286	283	280	277	274	271	268	265	262	259	256	254	251
64	307	304	301	298	295	292	289	286	283	280	277	274	271	268	265	262	259	256
66	315	312	309	305	302	299	296	293	289	286	283	280	277	273	270	267	264	261
68	323	320	316	313	309	306	303	299	296	293	289	286	282	279	275	272	269	266
70	331	328	324	320	317	313	310	306	303	299	296	292	288	285	281	278	274	271

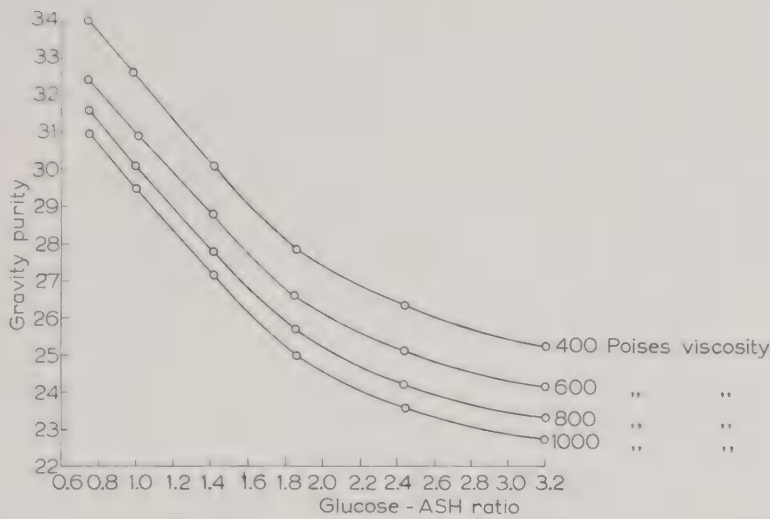


Fig. 12/1. Gravity purity and glucose-ash relationship at 400, 600, 800 and 1000 poises viscosity. Molasses saturated at 50° C.

Table 5 is based on the solubility determinations by VAN DER LINDEN and JACKSON and SILSBEE².

TABLE 5

THE FIGURES OF T. VAN DER LINDEN AND F. JACKSON AND C. GILLIS SILSBEE

purities																	Temp in °C
52	60	58	56	54	52	50	48	46	44	42	40	38	36	34	32	30	
74	172	170	168	166	164	162	160	158	156	154	152	150	148	146	144	143	26
76	174	172	170	168	166	164	162	160	158	156	154	152	150	148	146	145	28
79	177	175	173	171	169	167	164	162	160	158	156	154	152	150	148	147	30
82	180	178	176	174	172	170	168	166	164	162	160	158	156	154	152	150	32
86	184	182	180	177	175	173	171	169	167	165	163	161	159	157	156	154	34
89	187	185	183	181	179	177	174	172	170	168	166	164	163	161	159	158	36
93	191	189	186	184	182	180	178	176	174	172	170	168	166	165	163	162	38
96	194	192	190	188	186	183	181	179	177	175	173	171	170	168	167	166	40
200	198	196	194	192	190	187	185	183	181	179	177	176	174	173	172	171	42
205	203	200	198	196	194	192	189	187	185	183	181	180	178	177	176	176	44
209	207	205	203	200	198	196	194	191	189	187	186	184	183	182	181	180	46
213	211	209	207	204	202	200	198	195	193	191	190	188	187	186	185	185	48
218	216	213	211	209	206	204	202	199	197	195	194	192	191	190	190	190	50
223	220	218	215	213	211	208	206	204	202	200	198	197	196	195	194	194	52
227	224	222	219	217	215	212	210	208	206	204	202	201	200	199	199	199	54
231	229	226	224	221	219	217	214	212	210	208	207	206	205	204	203	202	56
236	233	231	228	226	223	221	218	216	214	213	211	210	209	209	208	208	58
240	237	235	232	230	227	225	222	220	218	217	215	214	213	213	213	212	60
245	242	239	237	234	231	229	227	225	223	221	220	219	218	218	218	218	62
249	247	244	241	238	236	233	231	229	227	226	225	224	223	223	222	222	64
254	251	248	245	242	240	237											66
259	256	253	250	247	244												68
264	261	257	254	251													70

The solubility of sucrose in saturated final molasses, containing varying amounts of invert sugar and inorganic nonsugars, has been determined by the Experiment Station of the Hawaiian Sugar Planters Assoc., in Honolulu⁸.

The object of these studies was to determine the exhaustibility of final molasses in the Hawaiian Islands. The combined influence of invert sugar and inorganic nonsugars on the solubility of sucrose in final molasses is expressed quantitatively by the glucose/ash ratio. Fig. 12/1 shows how, according to Hawaiian studies, the solubility varies with the glucose/ash ratio. The higher this ratio, the lower the solubility of sucrose, and the better the exhaustibility of the final molasses.

3. The Rate of Crystallization of Sucrose

The rate of crystal growth of sucrose, *i.e.* the quantity of sucrose crystallizing per unit time per unit of crystal surface, is determined mainly by two factors; firstly the rate of diffusion of the sugar molecules to the faces of the crystals, and secondly the rate of attaching the sucrose molecules into the crystal lattice.

KUCHARENKO and co-workers⁹ suggested that the crystallization process is controlled by the rate of diffusion only, and is a purely physical phenomenon. He neglected the second factor, assuming that the attaching of the molecules to the lattice of the crystal faces is very rapid in comparison with the rate of diffusion. For a diffusion-controlled process the law of FICK is applicable:

$$ds = - D \cdot q \cdot \frac{dc}{dx} dt$$

where ds is the quantity of material diffused across a cross-section of q in a time dt under a concentration gradient of $\frac{dc}{dx}$, where dx is a short distance.

The value of the diffusion coefficient D is given by the relation of Einstein-Stokes:

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$$

where

R = gas constant

T = absolute temperature

N = Avogadro's number

r = molecular radius of the diffusing substance

η = viscosity of the solution

NOYES and WHITNEY¹⁰ assumed that the diffusional resistance is confined to a comparatively thin film surrounding the crystallizing solid, since convection currents equalize the concentration in the bulk of the liquid. Low viscosity and vigorous stirring attenuate the film, decrease the diffusional resistance and will increase the rate of crystal growth; while high viscosity and poor agitation will decrease the rate of crystal growth because the diffusion layer will then be relatively thick and the diffusion process accordingly slow. NOYES and WHITNEY assumed the rate of crystal growth to be proportional to the crystal area Q and to the concentration gradient $C - C_s$:

$$\frac{dc}{dt} = K \cdot Q (C - C_s)$$

where

$\frac{dc}{dt}$ = rate of crystal growth

C = concentration in the bulk of the solution

C_s = saturated concentration of the solution
at the interface of crystal and solution

K = a proportionality constant

It is assumed that the rate of diffusion controls the process so that $K \cdot Q$ must be proportional to D or

$$K \cdot Q = f \cdot (D) = f \left(\frac{RT}{N \cdot 6\pi\eta r} \right)$$

KUCHARENKO determined the rate of crystal growth in pure sugar solutions for a degree of supersaturation up to about 1.1 and temperatures up to 70°C. The degree of supersaturation of the solution was expressed in a different way as

$$\frac{\text{sugar \% solution at } t^\circ \text{ C}}{\text{sugar \% saturated solution at } t^\circ \text{ C}}$$

In contrast with KUCHARENKO, VANHOOK¹¹ suggested that the rate of crystal growth is controlled by the second factor, resp. the fitting of the molecules into the crystal structure. The diffusional resistance is negligible in comparison with the transfer of sucrose molecules from the dissolved state into a solid state. He showed that the data of KUCHARENKO, with the concentration expressed in a molecular form, are in good agreement with first-order interfacial reaction with an operating factor accelerating the rate of crystallization at higher supersaturations and temperatures.

Very good results and simple mathematical equations were obtained using 'activities' or 'effective concentrations' instead of molecular concentrations. The rate of crystal growth can be expressed as

$$\text{vel.} = K(a - aMM)$$

where

K = specific reaction rate constant per unit reference area

a and aMM = 'activities' of the sugar solutions, resp. the saturated sugar solution.

From data in the literature the activities can be calculated for concentrations to the saturation points and for temperatures of 0–70° C.

VANHOOK presumed it not unreasonable to extend the calculations for concentrations in the supersaturated region.

If the rate of crystal growth is controlled by a first-order reaction, it is independent of the viscosity and the stirring intensity of the sugar solution.

VANHOOK added gum acacia to a supersaturated solution of sucrose, so that the viscosity was four and twentyfive times the viscosity of the pure solution; the rates of crystallization were 98, resp. 99% of that of the pure solution. This means that within the experimental error there was no effect of the viscosity.

DOSS and GHOSH¹² investigated the rate of growth of sucrose crystals suspended and rotated in a solution of constant supersaturation at 35 and 75.5° C.

The addition of carboxy methyl-cellulose to the solution, thereby increasing the viscosity ten-fold, hardly effected the rate of crystal growth; however caramel increasing the viscosity by 10% decreased the crystallization rate 20%.

Thus certain types of impurities affect the crystal growth far more than a high viscosity caused by viscous high molecular substances.

AFFERMI¹³ showed that nitrogen compounds inhibit the rate of crystallization of sucrose. The inhibitory effect decreases in the sequence: aspartic acid, glyocol, asparagine, leucine, betaine and trimethylaminechloride. The inhibitory effect of all these substances increases with their concentration up to about 4–6%. A higher nonsugar concentration produces no additional retarding effect on the rate of crystallization. A mixture of the nitrogen compounds in the proportions in which they occur in beet molasses added to a supersaturated solution of sucrose shows that the inhibitory effect closely resembles that obtained with pure aspartic acid. This seems to identify this substance as one of the principle inhibitors of the crystallization rate in beet syrups. However, although the rate of crystallization may

are retarded specifically by the nitrogen containing nonsugars, the end results are not so wide apart. In the presence of lime the nitrogen compounds, which have an acid character, lose much of their inhibitory power, whereas those of basic or neutral character, like betain and trimethylamine which do not combine with lime, lose none of their crystallization-hindering properties and maintain relatively the strongest inhibitory effects.

VANHOOK¹⁴ investigated the effect of both electrolytes and non-electrolytes, especially those found in natural cane and beet juices, *e.g.* K_2SO_4 , amino acid-salts, aconitates, invert sugar, betaine, raffinose, pectins, etc., on the rate of sucrose crystallization. He studied combinations of these contaminants imitating natural massecuites and concluded that generally all these materials depress the rate of crystal growth.

SMOLENSKI and ZELAZNY^{15, 16} determined the time required to throw out 75% of the crystallizable sucrose from solutions with different purity at the same temperature. They found primarily a large depressing effect on the rate of crystallization of sucrose caused by lowering the purity, resp. an increase in the nonsugar concentration.

They found that the rate of sucrose crystallization in a solution of 95 purity is about one half and in a solution of 80 purity is about one ninth of that of a pure sugar solution for the same supersaturation.

SILIN¹⁷ showed that the rate of crystallization of sucrose in a beetsugar solution of 55 purity is about 64 times slower than in a pure solution.

VANHOOK suggested that the rate of stirring had only a slight effect on the rate of crystallization. Carefully constructed observations on the effect of the intensity of stirring on the rate of crystal growth confirm the idea that diffusion in solutions of purities above 90 is more rapid than growth and therefore is not rate determining.

DOSS and GHOSH¹² showed that the rate of rotation of a crystal of sucrose from 2 to 11.5 r.p.m. in high purity solutions had no effect on the rate of crystal growth.

VANHOOK¹¹ showed that the increase of the rate of crystallization with the temperature at a given supersaturation is higher than would be anticipated for a diffusion process, but is consistent with a first-order reaction.

He concludes that a complete examination of the diffusion rate of sucrose at high concentrations would decide whether the controlling step in the crystallization might be an ordinary physical process or an 'activated' one.

If the rate of diffusion is neglected, the viscosity and rate of stirring of the solution have a secondary effect on the rate of crystallization in practical processes. In cooling of massecuites the heat transfer rate determining the

decrease in temperature per unit of time is influenced by the viscosity and the rate of stirring.

The motion of the solution (mother liquor) relative to the crystals is dependent on the rate of stirring of the solution.

The theory of the rate of crystallization is not far enough advanced to state in positive terms how the practical crystallization must be conducted. The published data only have a qualitative value for sugar house practice.

TABLE 6

RATE OF CRYSTALLIZATION FOR STANDARD LOW RAW FILLMASS AT VARIOUS SUPERSATURATIONS AND TEMPERATURES

Temperature °C	Crystallization rate (g/sq. m./h) at supersaturation of					
	1.22	1.28	1.39	1.49	1.51	1.59
65	2.10	—	—	—	—	—
64	1.50	—	—	—	—	—
63	—	2.35	—	—	—	—
62	1.17	2.15	—	—	—	—
60	1.02	1.82	—	2.49	—	—
58	0.88	1.53	—	2.46	—	—
56	0.76	1.34	—	2.43	—	—
54	0.65	1.19	2.01	2.40	—	—
52	0.54	1.04	1.66	2.38	—	—
50	0.42	0.89	1.49	2.35	2.35	—
48	—	0.73	1.36	2.32	1.93	1.61
46	—	0.58	1.24	2.29	1.57	1.32
44	—	0.44	1.13	2.26	1.29	1.06
42	—	—	1.04	2.24	1.09	0.84
40	—	—	0.97	2.21	0.90	0.66
38	—	—	0.89	2.18	0.76	0.53
36	—	—	0.83	2.14	0.64	0.43
34	—	—	—	2.11	0.55	—
33	—	—	—	2.09	—	—

MCGINNIS and SOMERS MORE¹⁸ determined the rates of crystallization at various temperatures and supersaturations for the crystallization of low purity raw beetsugar fillmass, which are of importance for the control of rapid crystallizers. The figures given in Table 6 show an optimum rate of crystallization for a degree of supersaturation of about 1.5. The supersaturation is expressed as

$$\frac{\text{sugar \% water at } t^{\circ} \text{ C}}{\text{sugar \% water at saturation at } t^{\circ} \text{ C}}$$

This optimum may be explained in two ways:

(1) If the crystallization process is controlled by the rate of diffusion, the rate is proportional to the degree of supersaturation and inversely pro-

portional to the viscosity of the solution. For a degree of supersaturation exceeding 1.5 the increase of viscosity will be greater than the increase in supersaturation and the rate of crystallization decreases.

(2) If the crystallization process is controlled by a first-order interfacial reaction, the optimum value may be caused by a decrease of the 'activity' of supersaturated solution with the increase of the concentration of sucrose. The figures of the table are remarkable because they show that at a certain optimum supersaturation, the velocity of crystallization is quite appreciable, even in the low temperature ranges.

The value found for the supersaturation depends on the solubility table which is used. The absolute values, however, are not so important. By careful analyses under known operational conditions, the optimum supersaturation may be found for practical sugar house work.

4. History of the Crystallizer Station

In the early years of the sugar industry it was common practice to discharge the contents of the vacuum pans into open storage tanks whether being grained boilings or concentrated molasses. The mass was left to itself to cool and crystallization of sucrose took place. Generally it was accepted that motion would disturb crystallization and prevent the formation of a uniform and large size grain. By the absence of any circulation, however, a great deal of the crystallizing sucrose was not deposited on the crystals already present, but local oversaturation was responsible for the spontaneous formation of fresh crystal nuclei.

The so called false grain left the centrifugals with the molasses and was lost in the final molasses. The crystal yield gained by crystallization resulting from undisturbed cooling was not what it is under proper technological conditions. In the last century, sugar was already obtained by a graining process in the vacuum pan, where crystallization certainly occurred in motion. It was not consistent to assume that motion would disturb crystallization in a sugar solution subject to cooling.

In 1884 WULFF in Germany obtained a most fundamental patent in which his ideas about crystallization in motion and simultaneous cooling were described. From here on the gradual introduction of crystallizers provided with stirring equipment started in the sugar industry over the whole world. The introduction of crystallization in motion was a step forward in sugar manufacture.

The advantage of stirring is that the massecuite is kept in uninterrupted motion so that the sugar crystals move freely in the mother liquor and

come continually in contact with still unexhausted supersaturated molasses. The sucrose in supersaturated condition can crystallize on the existing crystals and will have less tendency to form new nuclei. The stirring mechanism also assures a more even temperature in the crystallizer, as the massecuite cooled off against the outer wall is mixed regularly with the warmer massecuite in the center.

5. Types of Crystallizers and Cooling Systems

A concise review will be given of some of the many crystallizer types and cooling systems which have been proposed and used in the sugar industry during the course of past years.

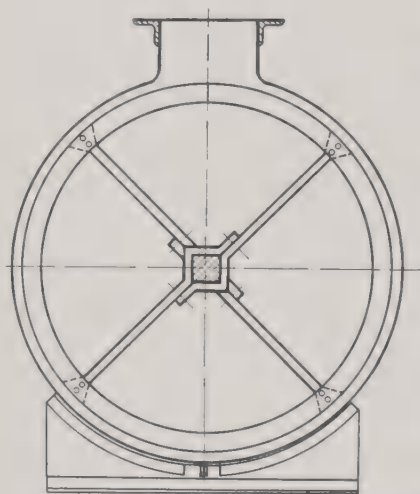


Fig. 12/2. O-type crystallizer.

Most commonly used and found in almost every sugar factory are the O- and U-shaped crystallizers as represented by Figs. 12/2 and 12/3. They are provided with a stirring gear in the form of a helix which slowly revolves in the massecuite. Heat exchange to the surrounding air is slow. The helix sweeps at some distance of the crystallizer wall so that with high purity massecuite a crust of sugar crystals will be formed against the inner wall decreasing the heat exchange.

If the helix would nearly touch the wall, sugar crystals would be pulver-

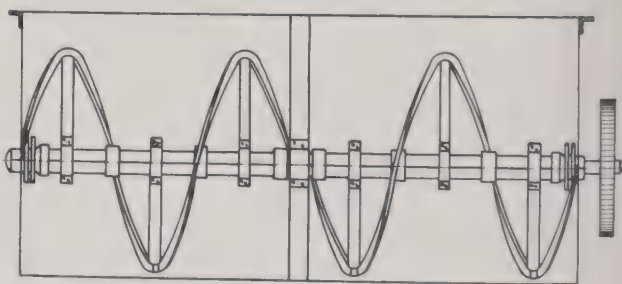
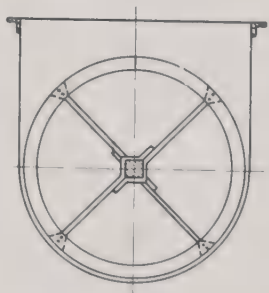


Fig. 12/3. U-type crystallizer.

ized, which is not permissible under any condition. The desirability to shorten cooling time has brought into existence a great number of cooling systems mostly using water as a cooling medium. It must be stressed that cooling systems have been not always constructed taking into account the high mechanical forces, which must be overcome when the heat ex-

change surfaces revolve in cooled massecuite of stiff consistency. In many cases this leads to breakdowns and water leakages which destroy the effect of cooling. Forced cooling of massecuite can be effected either by air or by water as a cooling medium. The water cooled type is mostly in use. The following water cooled systems can be distinguished.

(a) *Water cooling along the outside wall of the crystallizer shell.* As may be seen from Fig. 12/4 the outside wall of the crystallizer is cooled by a thin water film which flows over the whole length of the crystallizer wall. This construction is inexpensive but not efficient when short cooling times are desired. It is still in use in many sugar factories. The outer shell must be cleaned periodically because formation of algae and depositions of impurities from the cooling water will diminish the heat transfer. It must be mentioned in this respect that a water-jacketed crystallizer must be condemned since cleaning in most cases will be practically impossible. After some time the water-jacketed crystallizer will be transformed in a heat insulating rather than a heat exchanging surface.

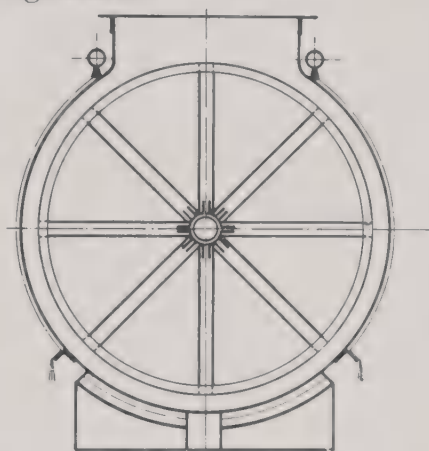


Fig. 12/4. Crystallizer cooled along outside wall.

(b) *Stationary tubes.* Two examples of this type are illustrated in Figs. 12/5

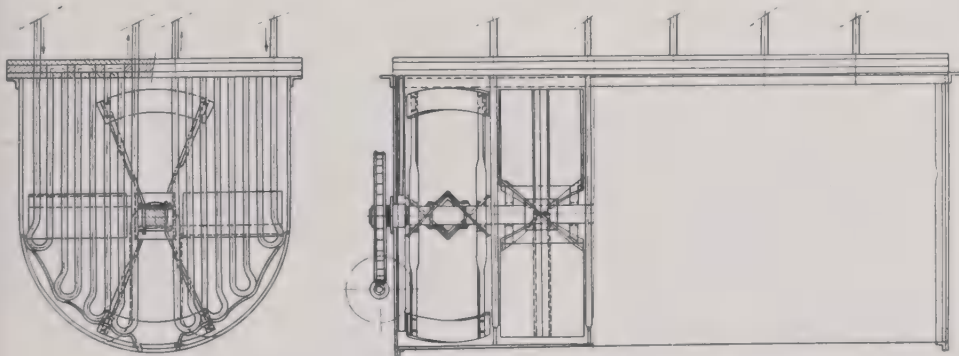


Fig. 12/5. Cooling system with stationary tubes. (VOLKERT)

and 12/6. The cooling tubes have a fixed position and several nests of these tubes can be distributed over the whole length of the crystallizer. In the spaces between the nests, paddles are revolving in order to keep the massecuite in motion thus preventing the danger of local overcooling. The cooling

surface that can be installed is comparatively small and short cooling cycles cannot be expected.

(c) *Revolving tubes.* Some constructions are shown in Figs. 12/7, 12/8 and 12/9. Many more cooling systems of the revolving tube type exist, most of which have in common that on rotation through the massecuite the cooling

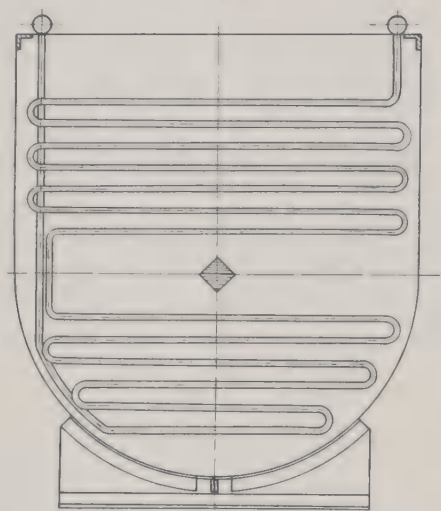


Fig. 12/6. Cooling system with stationary tubes. (KOPKE)

system will encounter a high resistance especially in the lower temperature ranges of low purity massecuites. They should therefore be of a sturdy construction to prevent breakdowns and water leakages caused by deformation of joints and flanges.

(d) *Stationary discs.* A type of this cooling system, which is not so common as the tubetype, is illustrated in Fig. 12/10. Half the number of cooling elements is adjustable in a vertical sense in order to fix these elements in the most favorable position. The massecuite is forced to flow alternately underneath and over the top of the cooling elements, while paddles between

the elements take care of the motion in the massecuite. This crystallizer may be used either as an intermittent or a continuous type. An attempt has been made to prevent incrustations of sugar on the cooling elements by using scrapers sweeping along the discs.

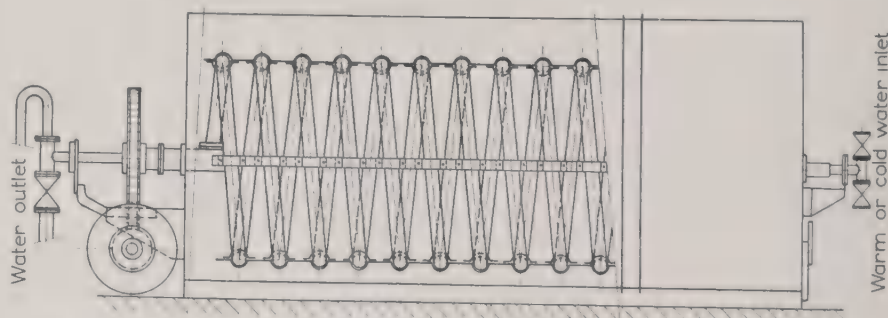


Fig. 12/7. Cooling system with revolving tubes. (RAGOT-TOURNEUR)

(e) *Rotary discs.* In Fig. 12/11 a rotary disc type is shown. On rotation the thin cooling elements will cut through the massecuite and therefore encounter a small resistance. This type of crystallizer is used mostly in a continuous way, cooled water being applied in counter-current.

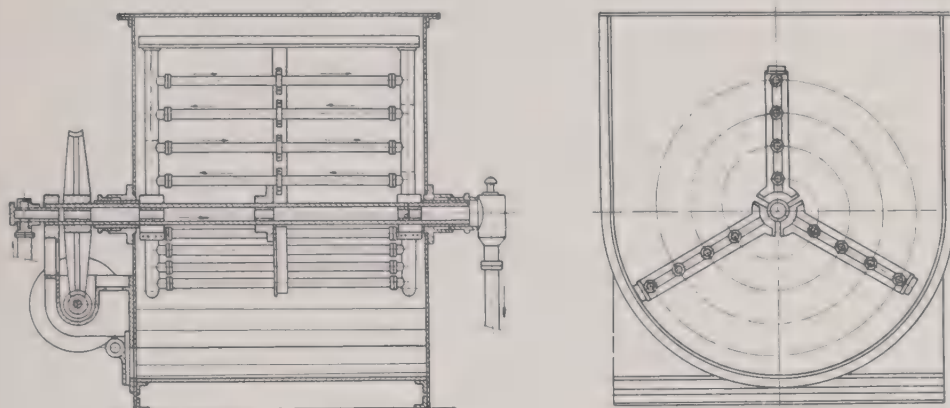


Fig. 12/8. Cooling system with revolving tubes. (KARLIK-CZAPIKOWSKY)

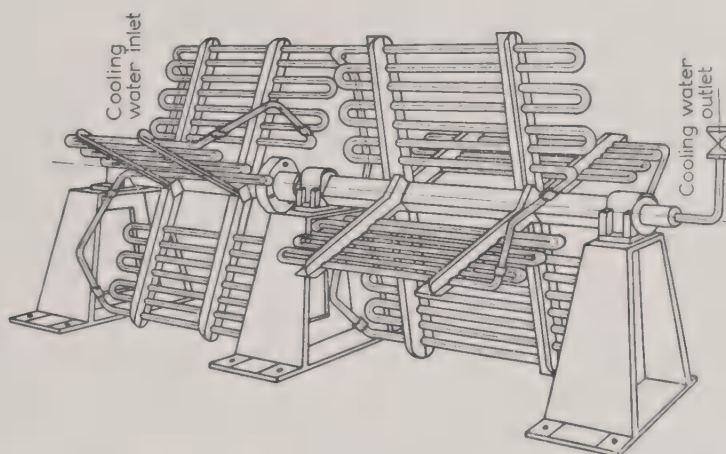


Fig. 12/9. Cooling system with revolving tubes. (HERRISON)

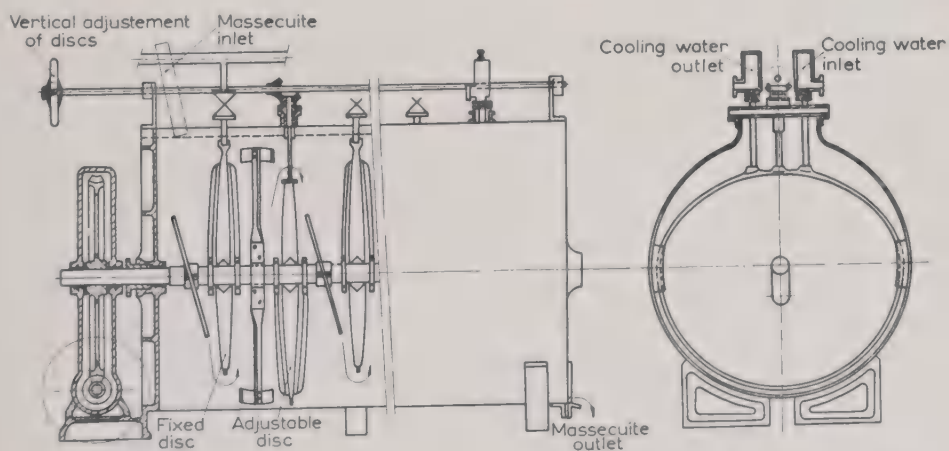


Fig. 12/10. Cooling system with stationary discs. (Ned. Ind. Industrie)

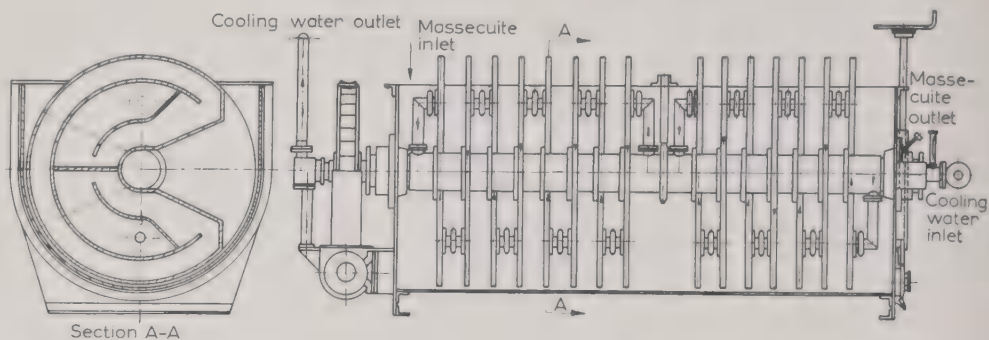


Fig. 12/11. Cooling system with revolving discs. (Werkspoor)

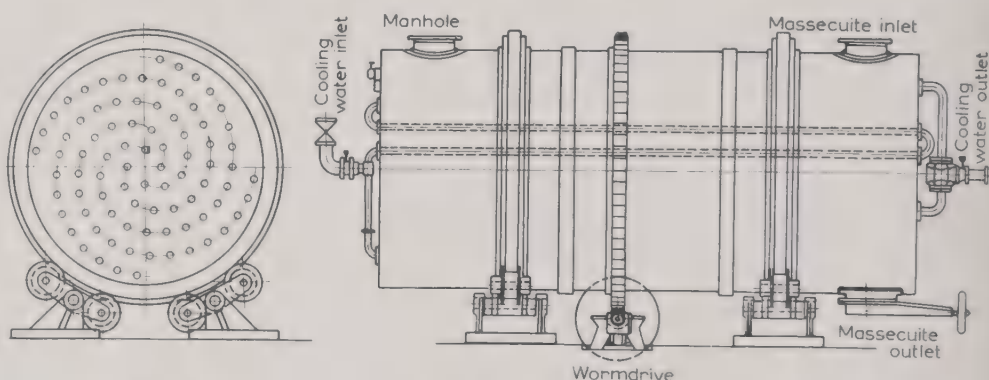


Fig. 12/12. Revolving crystallizer with stationary tubes. (LaFeuille)

(f) *Revolving crystallizers.* The crystallizer as shown in Fig. 12/12 is provided with stationary cooling tubes. By the revolving action of the whole crystallizer a good mixing of the massecuite is realized.

6. Construction Material and Shape of Cooling Elements

In most cases the construction material used for stationary and moving cooling elements is steel. The objection against the use of steel is that it is subject to corrosion, which in the long run will greatly diminish the heat transfer. Although the cost of non-corrosive materials is higher, it is always worth while to consider the advantages of using such materials. If steel is used, it is recommendable to coat tubes or discs with a corrosion resistant layer, as *e.g.* by tinning.

The shape of cooling elements is important in view of the resistance being encountered by the cooling elements revolving in the massecuite. Revolving discs show for the same heat transfer area far less resistance than revolving tubes, especially when these are mounted parallel to the axis of rotation. In such a case it would be an improvement to use tubes of an elliptic shape

instead of cylindrical tubes, such as proposed by HONIG^{18a}. Apart from smaller resistance, it is also claimed that the heat transfer would be increased.

7. Heat Transfer Coefficients for Different Types of Massecuite

The professional sugar literature does not contain a great number of data on heat transfer and heat transmission coefficients in crystallizers. The Experiment Station for the Java sugar industry determined the total heat transfer for massecuites of high purity (over 70) in two different types of crystallizers, using water as a cooling medium. They were both newly installed and had perfectly clean surfaces, free from scale and corrosion products on the massecuite as well as on the water side. The two systems used were the LAFEUILLE and the WERKSPoor crystallizer. As standards for the average total heat transfer in massecuites with a purity higher than 70 in a temperature range of the massecuite of 70–40° C was found 30–50 cal/sq. m/°C/h. The greatest value has been found for the highest temperatures of the massecuite to be cooled.

VENTON¹⁹ determined overall coefficients of heat transfer in WERKSPoor crystallizers, treating final massecuites of about 60 purity. He reports the following figures (Table 7).

TABLE 7

OVERALL COEFFICIENTS OF HEAT TRANSFER IN WERKSPoor CRYSTALLIZERS

Factory	Overall heat transfer coefficient cal/sq. m./°C/h	R.p.m. of cooling elements
MORETON	24	0.3
PLANE CREEK	98	0.8
PLANE CREEK	73	0.5

The rotating speed of the cooling elements has a significant influence on the heat transfer coefficient.

BRUNELLI²⁰ determined the overall heat transfer coefficient in a WERKSPoor crystallizer, treating final beet massecuites, and found average figures of 25 cal/sq. m/°C/h.

BERGÉ and STORMS²¹ report an overall heat transfer coefficient of 25 cal/sq. m/°C/h in a water cooled crystallizer equipped with stationary U-tube cooling tubes treating final massecuites.

HONIG²² calculated the average overall heat transfer coefficients for different types of heat exchange surfaces that can be distinguished in modern

crystallizers, treating after product boilings in cane sugar mills (purities 58–62), and arrived at the conclusions as shown in Table 8.

TABLE 8

AVERAGE OVERALL HEAT TRANSFER VALUES (IN CAL/SQ. M./°C/H) OF DIFFERENT TYPES OF HEAT EXCHANGE SURFACES IN CRYSTALLIZERS FOR *C*-BOILINGS, OUTSIDE AIR TEMP. 25–30° C, TEMP. COOLING WATER 25° C

Temp. level in °C massecuite in crystallizers to be cooled	Outside wall/ still air	varies from	Massecuite surface/ still air	varies from	Outside wall/ water spray	varies from	Moving cooling tube
70	3	(2–5)	5	(4–10)	7	(5–1)	40
65	2.7	(2–5)	5		7		30
60	2.4	(2–5)	5		7		25
55	2.2	(2–4)	5		6		25
50	1.8	(1–3)	4		5		20
45	1.5	(1–3)	3		4		15

These values can be from 0.3 to 1.5 times the given figures, depending on the viscosity of the molasses to be cooled and on the form and the speed of rotation of moving cooling elements with clean surfaces. For stationary cooling tubes the data given in this column have to be multiplied by 0.3–0.4.

The data as given in Table 8 cannot be taken as absolute standards, as they will be influenced by a number of conditions existing at other sugar factories. They can be used, however, to calculate the heat transfer performance of crystallizer stations to be installed. The cooling effect of crystallizers can be increased by free circulating air, eventually a forced air circulation, and a perfect cleanliness of the outer and inner surfaces to prevent any kind of resistance against the flow of heat.

8. Speed of Rotation of Cooling Elements for Different Types of Massecuite

In most cases, the cooling elements revolving in the massecuite act at the same time as stirrers. It is to be doubted whether the speed of rotation and the rate of stirring between the limits as applied in practice have much influence on the rate of crystallization.

VANHOOK²³ in his studies about crystallization of sucrose comes to the conclusion that the rate of stirring has only a slight effect on the rate of crystallization.

TVERDOCHLEBOV²⁴ reported a case where the crystal yield was even increased by lowering the rotation speed of the crystallizer stirrer from 1 to

36 r.p.m. The object was to be able to treat massecuites of high viscosity which as a rule will have a low water content.

Rotation speeds in practice will vary from about 0.3–1.5 r.p.m.; the speed is mainly determined by the physical nature of the massecuite to be treated. As a rule, high purity massecuites with a low viscosity will allow higher speeds than low purity massecuites which, especially in the lower temperature range, can be very viscous.

There is, however, a definite influence of the speed of rotation of cooling elements on the heat transfer.

HONIG²⁵, using data collected at different sugar factories, has made calculations showing the relation between speed of rotation of cooling elements and transitional specific heat transfer: cooling element-massecuite. The figures arrived at are based on the same type of molasses (with a viscosity of ± 800 poises at 30°C and ± 170 poises at 40°C) at a temperature of 35°C and cooling water of $25\text{--}30^{\circ}\text{C}$. They are shown in Table 9.

TABLE 9

EFFECT OF RELATIVE SPEED OF COOLING SURFACES ON THE HEAT TRANSFER COEFFICIENT

Relative speed of cooling surface-massecuite in cm/sec	Heat transfer coefficient cal/sq. m./ $^{\circ}\text{C}/\text{h}$
0	13
0.8	22
1.6	29
2.5	34
3.3	40
5.0	46
6.7	53
8.3	60
10.0	63
11.7	67
13.3	70

With regard to a good heat transfer it is important to use rotation speeds as high as practically possible.

9. Crystallizer Drive and Power Consumption

In modern sugar factories every crystallizer should be driven by its own motor which must be provided with a watt meter. In this way a regular control on power consumption is possible. When the power consumption rises too high, massecuites can be diluted with water or diluted molasses in order to prevent breakdowns. As the heat transfer is influenced by the

speed of rotation of the cooling elements, it would be a technical advantage if each crystallizer were provided with a gearbox with variable speed so that the rotation speed of the cooling elements could be adapted to the changing condition of the massecuite during the cooling process. The higher speeds could be used in the beginning, while lower speeds could be applied when the power consumption is rising. This method does not apply to continuous cooling methods where conditions, once the system is operating, will be more or less constant.

In the literature the following data are given for the required power to be installed per 100 hl crystallizer content.

NOEL DEERR ²⁶	0.30–0.35 h.p.
TROMP ²²	0.6–1 h.p.
HUGOT ²²	0.66 h.p.
EMMEN ²²	0.5–1 h.p.
HONIG-ALEWIJN ³⁰	0.5–3 h.p.

For high purity boilings 1 h.p./100 hl as power to be installed will be sufficient. With the existing tendency to obtain a better exhaustion of the final molasses by reducing the water content as much as possible, the power to be installed for crystallizers treating final massecuites may even exceed the highest above mentioned figure. HONIG³¹ has given the following formula by which it is possible to make a fairly accurate estimate of the power consumption of crystallizers using cooling systems:

$$\text{power consumption in horse power} = \frac{(r_{m1} \times O_1 + r_{m2} \times O_2) \times n \times P}{4.2 \times 10^{12}}$$

wherein

- r_{m1} = mean distance of heat exchange elements from axis of rotation in cm
- O_1 = heat exchange surface in sq. cm
- n = number of rotations of heat exchange element per hour
- r_{m2} = mean distance of stirring elements in cm
- O_2 = surface of stirring elements in sq. cm
- P = viscosity of massecuite (molasses) to be cooled in poises.

10. Crystallizer Control and Control Instruments

A careful control at the crystallizer station is essential in order to judge the efficiency of the crystallizers. Certain data must be collected and recorded at regular intervals.

(a) *Supersaturation*. The main value which will give an indication of the behavior of a sugar solution subject to crystallization is the degree of super-

saturation. In modern pan boiling it has become a firmly established practice to guide the boiling process by constant determination and recording of the supersaturation. The same should be done in guiding the crystallization process in the crystallizer. The rate of cooling should keep pace with the rate of crystallization. Too rapid cooling may lead to false grain formation or result in a high supersaturation with a reduction in the rate of crystallization. Too slow cooling may result in a rate of crystallization not optimum for good factory efficiency.

The supersaturation can easily be determined indirectly by measuring the electric conductivity. It is advisable to provide each crystallizer with an electric conductivity meter. In order to be able to interpret the conductivity data into degrees of supersaturation, from time to time a determination of the supersaturation should be made in the laboratory. This can be done by taking a sample of the mother liquor from the crystallizer *e.g.* by means of a 'nutsch' or separated in a laboratory centrifugal. The temperature at the time of sampling must be taken, the molasses analysed in the laboratory for sucrose content, brix and purity, and with the aid of a solubility table the supersaturation can be calculated.

A rapid method to determine the supersaturation is the use of the saturoscope. With this instrument the saturation temperature of a molasses can be measured.

Although slightly incorrect, it can be assumed for practical purposes that the relative solubility of sucrose at different temperatures is constant for solutions of different purities. When the saturation temperature of a given solution is known the supersaturation can be calculated by the ratio

$$\frac{\text{solubility of pure sucrose at saturation temperature}}{\text{solubility of pure sucrose at actual temperature}}$$

The saturoscope is also used for the determination of the temperature to which a massecuite can be heated safely before the centrifugal process.

A record kept about conditions of supersaturation during the cooling process is important because it will enable one to determine in practice at which limit the supersaturation should be kept to obtain a maximum after crystallization.

(b) *Viscosity*. A knowledge of this value is important because the viscosity of a massecuite has an influence on the power consumption as well as on the heat transfer. Viscosities should be determined at the different stages of the cooling process. In this way standard data for the operational conditions regarding concentrations to be maintained can be obtained.

Determination of the viscosity can be done with available commercial equipment by direct measurement of the massecuite in the crystallizer, *e.g.* the BROOKFIELD viscosimeter.

The viscosity can also be estimated indirectly by electric conductivity measurement, as there exists a simple relationship between viscosity and electric conductivity. The readings of a conductivity meter will provide an indication to warn the supervising personnel that the cooling process has to be stopped, respectively to be alternated by reheating, or that dilution of the massecuite has to be applied in order to prevent breakdowns or damage to the cooling system.

(c) *Temperatures.* During the cooling and heating process the temperature of the massecuite should be noted at regular intervals as well as the inlet- and outlet temperature of the cooling water.

(d) *Power consumption.* The driving motor of a crystallizer should be provided with a watt meter so that the power consumption can be noted at regular intervals.

11. Maintenance of Cooling Systems in Crystallizers

As with outside cooling water oxygen is introduced, the inside of the cooling elements will be subject to corrosion when steel is used as construction material. Corrosion products will greatly decrease the heat transfer and it is important to prevent corrosion as much as possible. It is advisable to apply a closed cooling water system in which water is used having a sufficient amount of soda to raise the pH over 10. At this alkalinity the corrosion of iron is reduced considerably and becomes practically insignificant. When a closed cooling water system is used, the heat in the circulating cooling water should be removed by a heat exchanger, for which outside cooling water must be applied. This cooling water will by its nature be aggressive towards iron and steel. This heat exchanger for the circulating cooling water can be inexpensive and simple in construction. Care must be taken, however, that mechanical and chemical cleaning of the heat exchange surfaces can be performed easily. When no closed cooling system is used the inside of the cooling elements should be cleaned periodically. Since many cooling elements are not easily accessible for mechanical cleaning, the iron oxide scale can be removed by circulating a diluted acid to which an inhibitor is added through the elements. For scale removal the inside of the cooling system can be washed with hot soda or detergent solutions, circulating at high speeds. To a certain extent the formed scale will be loosened and

most carried away with the circulating liquid. This will give only a partial effect because the corrosion or scale will not be removed completely.

HONIG³² advises considering the possibility of preventing corrosion in water cooled systems by a so-called cathodic protection, which has been found practicable for prevention of corrosion in boilers. After the campaign or when the cooling system is not in use for a long time, the cooling water remaining in the cooling system should be drained. Provisions should be made that this can be executed easily.

12. Time Needed for the Efficient Cooling of Different Types of Massecuite

The higher the purity of a massecuite, the higher will be the crystallization rate. High purity massecuites can be safely cooled in a short time with good crystallization results. For massecuites other than those giving final molasses, cooling times will vary from 3/4–4 hours depending on the purity.

There is no general agreement as to the rate of cooling for massecuites giving final molasses.

GILLET³³ of Crockett, Cal. (U.S.A.) recommends cooling times of 50–100 hours for refinery afterproducts. A cooling time of 80 hours is considered the minimum for a good molasses exhaustion in refineries. Crystallizers used in this case are the water-jacketed KILBY type.

BERGÉ and STORMS³⁴ in Belgium consider cooling times of 36 hours as practical maximum for refinery afterproducts. The molasses purity could not be lowered by cooling times longer than 48 hours. The massecuites are cooled in crystallizers equipped with stationary tubes.

BRUNELLI³⁵ in Italy recommends cooling times of 20–24 hours for beetsugar afterproducts, using the WERKSPoor type continuous crystallizer.

VENTON³⁶ in Australia, in experiments with continuously working WERKSPoor crystallizers for cane sugar afterproducts, reports cooling times of 9–13 hours with satisfactory results on molasses exhaustion.

MCGINNIS³⁷ advocates that for beetsugar massecuites during the cooling process a supersaturation be maintained of which the upper limit is set by false grain formation. He states that it is difficult to maintain this optimum supersaturation with water-jacketed crystallizers. His experience shows that by faster cooling crystallization rates may be accelerated as much as five or six times.

Short cooling times can only be applied with cooling systems having sufficient cooling surface per unit of massecuite.

13. Reduction in Total Massecuite Quantity by Rapid Cooling of First Boilings. Simplification of Boiling Scheme

In experiments carried out by HONIG and ALEWIJN⁸⁸ with rapid cooling of high purity massecuites, it was shown that the purity of the molasses was 5 degrees lower than when these massecuites were cooled for 3 hours in ordinary air cooled crystallizers.

The effect of rapid cooling of *A*-massecuite on the total massecuite quantity can be shown from the following calculation based on actual factory practice.

Starting from the same analysis figures of boiling house products and using the same method of working, a four boiling scheme using ordinary air cooled crystallizers has been compared with a three-boiling scheme using rapid cooling crystallizers for *A*-massecuite.

TABLE 10
ANALYSIS OF BOILING HOUSE PRODUCTS

	Four massecuite system			Three massecuite system		
	brix	purity	specific weight	brix	purity	specific weight
Syrup	60	84.3	1.29	60	84.3	1.29
<i>A</i> -massecuite	92	84.3	1.50	92	84.3	1.50
<i>A</i> -molasses	70	65.7	1.35	70	60.7	1.35
<i>B</i> -massecuite	94	72.8	1.51	—	—	—
<i>B</i> -molasses	70	53.5	1.35	—	—	—
<i>C</i> -massecuite	96	64.9	1.53	96	69.9	1.53
<i>C</i> -molasses	70	45.4	1.35	70	45.4	1.35
<i>D</i> -massecuite	98.2	57.1	1.54	98.2	57.1	1.54
Final molasses	97	29.3	—	97	29.3	—
Seed magma	87.8	84.3	—	87.8	84.3	—
<i>D</i> -sugar	99.3	84.3	—	99.3	84.3	—

(a) *Four-Boiling Scheme*

Straight boiling with 4 massecuites. The *D*-massecuite is started on a footing of *A*-molasses and syrup, with an apparent purity of 70. The *D*-sugar is mixed with syrup to form a seed magma. It is assumed that the purity of the *D*-sugar is equal to that of the syrup and that 80 parts of *D*-sugar are mingled with 20 parts of syrup.

Calculation. Starting from 100 tons of solids in syrup the amounts of *A*-, *B*-, *C*- and *D*-massecuites will be calculated. 100 tons solids in syrup will yield

$$\frac{84.3 - 29.3}{98.7 - 29.3} \times 100 = 79.3 \text{ tons solids in raw sugar.}$$

Solids in final molasses will be $100 - 79.3 = 20.7$ tons.

D-massecuite

$$\begin{aligned}
 \text{Solids in } D\text{-massecuite} &= 20.7 \times \frac{84.3 - 29.3}{84.3 - 57.1} = 41.9 \text{ tons.} \\
 \text{Solids in footing} &= 41.9 \times \frac{57.1 - 45.4}{70 - 45.4} = 19.9 \text{ tons.} \\
 \text{Solids in } C\text{-molasses} &= 41.9 - 19.9 = 22.0 \text{ tons.} \\
 \text{Solids } A\text{-molasses in footing} &= 19.9 \times \frac{84.3 - 70}{84.3 - 65.7} = 15.3 \text{ tons.} \\
 \text{Solids in syrup in footing} &= 19.9 - 15.3 = 4.6 \text{ tons.} \\
 \text{Solids in } D\text{-sugar} &= 41.9 - 20.7 = 21.2 \text{ tons.} \\
 \text{Volume of } D\text{-massecuite} &= \frac{41.9}{98.2 \times 1.54} \times 100 = 27.6 \text{ cu.m or 980 cu.ft.}
 \end{aligned}$$

21.2 tons solids in D-sugar will be mingled with $\frac{21.2}{80} \times 20 = 5.3$ tons

solids in syrup and will form $21.2 + 5.3 = 26.5$ tons solids in seed magma.

C-massecuite

$$\begin{aligned}
 \text{Solids in } C\text{-massecuite} &= 22.0 \times \frac{98.7 - 45.4}{98.7 - 64.9} = 34.7 \text{ tons} \\
 \text{Solids in } C\text{-sugar} &= 34.7 - 22 = 12.7 \text{ tons} \\
 \text{Solids in footing} &= 34.7 \times \frac{64.9 - 53.5}{84.3 - 53.5} = 12.8 \text{ tons} \\
 \text{Solids in } B\text{-molasses} &= 34.7 - 12.8 = 21.9 \text{ tons} \\
 \text{Volume } C\text{-massecuite} &= \frac{34.7}{96 \times 1.53} \times 100 = 23.8 \text{ cu.m or 840 cu.ft.}
 \end{aligned}$$

B-massecuite

$$\begin{aligned}
 \text{Solids in } B\text{-massecuite} &= 21.9 \times \frac{98.7 - 53.5}{98.7 - 72.8} = 38.2 \text{ tons} \\
 \text{Solids in } B\text{-sugar} &= 38.2 - 21.9 = 16.3 \text{ tons} \\
 \text{Solids in footing} &= 38.2 \times \frac{72.8 - 65.7}{84.3 - 65.7} = 14.6 \text{ tons} \\
 \text{Solids in } A\text{-molasses} &= 38.2 - 14.6 = 23.6 \text{ tons} \\
 \text{Volume } B\text{-massecuite} &= \frac{38.2}{94 \times 1.51} \times 100 = 27 \text{ cu.m or 960 cu.ft.}
 \end{aligned}$$

A-massecuite

$$\begin{aligned}
 \text{Solids in } A\text{-massecuite} &= (23.6 + 15.3) \times \frac{98.7 - 65.7}{98.7 - 84.3} = 89.2 \text{ tons} \\
 \text{Solids in } A\text{-sugar} &= 89.2 - (23.6 + 15.3) = 50.3 \text{ tons} \\
 \text{Solids in } A\text{-molasses} &= 89.2 - 50.3 = 38.9 \text{ tons} \\
 \text{Volume } A\text{-massecuite} &= \frac{89.2}{92 \times 1.50} \times 100 = 65 \text{ cu.m or 2300 cu.ft.}
 \end{aligned}$$

(b) *Three-Boiling Scheme*

Straight boiling with 3 massecuites. The same working method as for the four-boiling scheme, except that the *B*-boiling is omitted, while *A*-molasses is drawn into the *C*-massecuite. A rapid cooling crystallizer is used for the *A*-massecuite, and air cooled crystallizers for *C*- and *D*-massecuite. The purity of the *A*-molasses will be 60.7 instead of 65.7.

Calculation. Starting from 100 tons of solids in syrup, the amounts of *A*-, *C*- and *D*-massecuite have been calculated using the purities as obtained under factory conditions. Quantities of raw sugar and molasses are the same as for the four-boiling scheme.

D-massecuite

As for four-boiling scheme, except

$$\begin{aligned}\text{Solids in } A\text{-molasses in footing} &= 19.9 \times \frac{84.3 - 70}{84.3 - 60.7} = 12.1 \text{ tons} \\ \text{Solids in syrup in footing} &= 19.9 - 12.1 = 7.8 \text{ tons}\end{aligned}$$

C-massecuite

$$\begin{aligned}\text{Solids in } C\text{-massecuite} &= 22 \times \frac{98.7 - 45.4}{98.7 - 69.9} = 40.7 \text{ tons} \\ \text{Solids in } C\text{-sugar} &= 40.7 - 22 = 18.7 \text{ tons} \\ \text{Solids in footing} &= 40.7 \times \frac{69.9 - 60.7}{84.3 - 60.7} = 15.9 \text{ tons} \\ \text{Solids in } A\text{-molasses} &= 40.7 - 15.9 = 24.8 \text{ tons} \\ \text{Volume } C\text{-massecuite} &= \frac{40.7}{96 \times 1.53} \times 100 = 27.9 \text{ cu.m or } 989 \text{ cu.ft.}\end{aligned}$$

A-massecuite

$$\begin{aligned}\text{Solids in } A\text{-massecuite} &= (12.1 + 24.8) \times \frac{98.7 - 60.7}{98.7 - 84.3} = 97.5 \text{ tons} \\ \text{Solids in } A\text{-sugar} &= 97.5 - (12.1 + 24.8) = 60.6 \text{ tons} \\ \text{Solids in } A\text{-molasses} &= 97.5 - 60.6 = 36.9 \text{ tons} \\ \text{Volume } A\text{-massecuite} &= \frac{97.5}{92 \times 1.50} \times 100 = 71.2 \text{ cu.m or } 2520 \text{ cu.ft.}\end{aligned}$$

Table 11 gives a summary of the quantities of massecuite and sugar for the four- and the three-boiling scheme.

TABLE 11

SUMMARY OF QUANTITIES OF MASSECUTE AND SUGAR PER 100 TONS OF SOLIDS IN SYRUP

	Four-boiling scheme			Three-boiling scheme		
	cu. m.	cu. ft.	tons	cu. m.	cu. ft.	tons
A-massecuite	65	2300	—	71.2	2300	—
A-sugar	—	—	50.3	—	—	60.6
B-massecuite	27	960	—	—	—	—
B-sugar	—	—	16.3	—	—	—
C-massecuite	23.8	840	—	27.9	989	—
C-sugar	—	—	12.7	—	—	18.7
D-massecuite	27.6	980	—	27.6	980	—
	143.4	5080	79.3	126.7	4269	79.3

Reduction in total massecuite volume due to three-boiling scheme = 11.6%.
 The capacity of the boiling station will be increased accordingly. The two-boiling schemes are shown schematically in Figs. 12/13a and 12/13b.

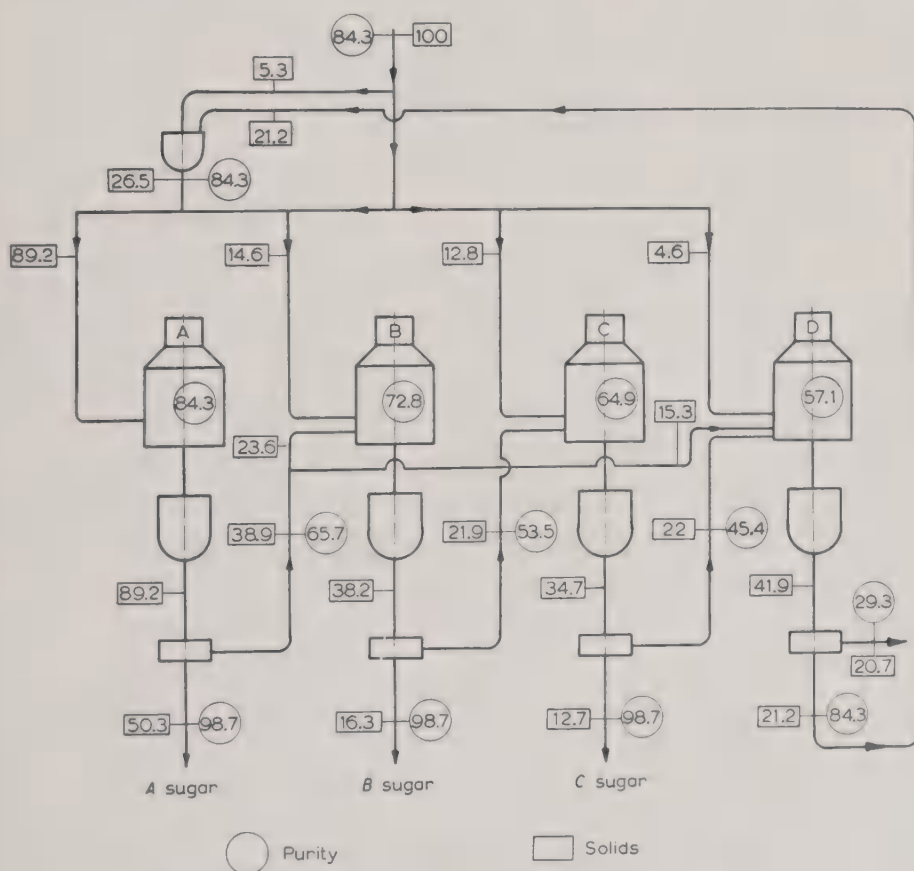


Fig. 12/13a. Four-boiling scheme with ordinary air cooled crystallizers.

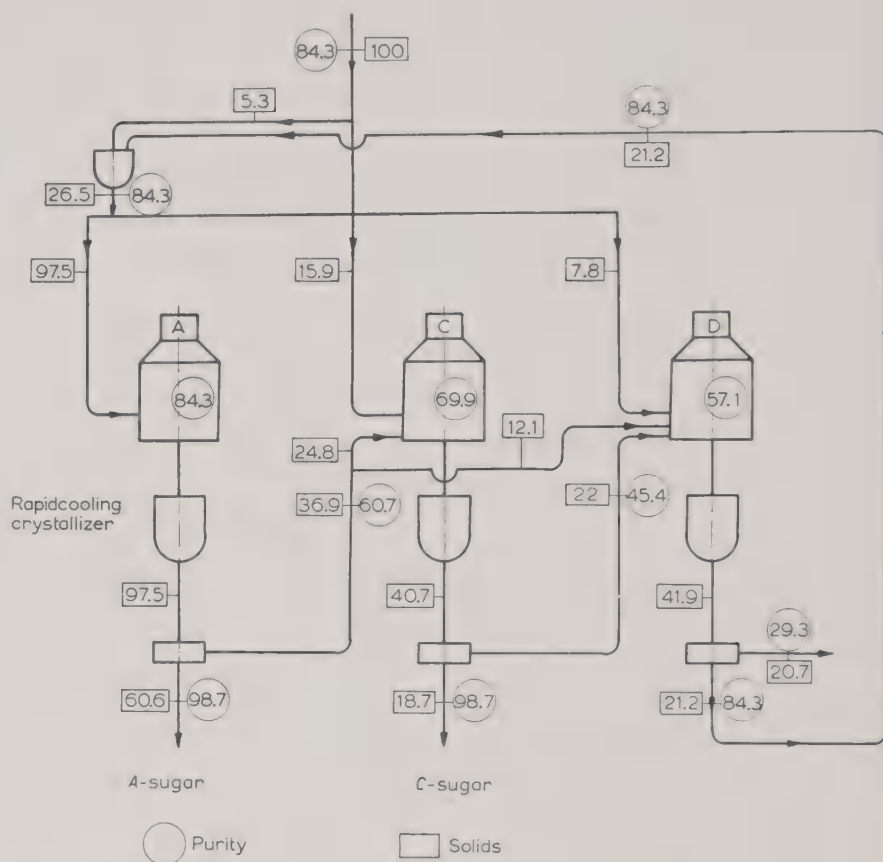


Fig. 12/13b. Three-boiling scheme with rapid cooling crystallizers for A-masseccuite.

14. Secondary Grain Formation in Crystallizers

When during the cooling process in high purity boilings the supersaturation rises to extreme values, fresh nuclei of sucrose will be formed. In batch coolers the danger exists that the temperature difference between masseccuite and cooling water is too high in the beginning of the cooling process. The cooling rate will be too fast resulting in formation of false grain. When the cooling system consists of stationary cooling elements, local overcooling may occur easily if insufficient mixing of the masseccuite by the stirring elements exists.

Continuously working cooling systems, where the cooling water can be applied in counter-flow with the masseccuite to be cooled, have the advantage that the temperature difference between masseccuite and cooling water is always low and constant during the entire cooling cycle.

False grain formation should be avoided under all conditions. HONIG and ALEWIJN³⁹ have shown that small crystals during the crystallization

process grow faster than large ones. On the other hand false grain formed in crystallizers will seldom grow to a size large enough for proper separation from the mother liquor in the centrifugals. Either curing in the centrifugals becomes difficult or the small grain will pass partly through the screen with the molasses. Thus the effect of aftercrystallization in the crystallizer is reduced and, in the case of final boilings, losses in final molasses will be increased.

15. Installation of Crystallizers. The Use of Massecuite Pumps

A crystallizer must be seen as a heat exchanger; it has to be installed in such a position that conditions for heat exchange are as favorable as possible. Sometimes, to save floor space, crystallizers are closely built together, directly placed on concrete floors and immediately under the vacuum pans. Under such conditions cooling times and cooling efficiency will be unsatisfactory.

Crystallizers can be placed on an open floor with grates to assist free air circulation. The distance between the crystallizers should be such that a good air circulation is always possible.

When the crystallizers are placed on the factory floor it is necessary to pump the cooled massecuite to the centrifugal mixers. Low purity massecuites especially can be very viscous and pumping becomes difficult when the viscosity of the massecuite and molasses is greater than 1500 poises. In many cases the massecuite is diluted with water to make pumping possible. The application of this practice introduces the danger of redissolution of sucrose and corresponding increased losses in final molasses. Crystallizers in which the massecuite cannot be reheated after the cooling process should be placed preferably at such a height that transport of the massecuite to the centrifugal mixer takes place by gravity.

If, after the cooling process, the massecuite can be reheated in the crystallizer to the saturation temperature of the mother liquor, the use of a pump is an acceptable technique in most cases because by heating, the viscosity of the massecuite will be reduced sufficiently to make pumping practically possible (viscosities of massecuite and molasses < 1500 poises).

With continuous cooling systems the possibility of reheating the massecuite at the end of the cooling cycle should exist; thereby facilitating pumping. The pumping of cooled last massecuite should be avoided, if possible, and after cooling the massecuite should be able to flow to the centrifugal mixer by gravity.

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CHAPTER 13

CONDITIONING OF MASSECUITES IN CRYSTALLIZERS

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1. Introduction

Crystallizer processing is a unit operation designed to permit massecuites which have been boiled to maximum workable consistency in a vacuum pan under near isothermal conditions to continue crystallization at progressively lowered temperatures. The basic driving force in the process is the supersaturation brought about by the decreased solubility of sucrose. Ultimately, however, for a given temperature, crystallization will cease at a state of equilibrium where the mother liquor is no longer supersaturated. The molasses from such a massecuite is called exhausted. The technical objective in crystallizer work, therefore, is to approach as closely as practicable this exhausted state in a minimum of time.

Prime considerations in the operations are that crystallization shall take place rapidly, that no new crystal nuclei be formed and that the massecuite finally be capable of ready separation of sugar and molasses in a centrifugal machine. The rate of crystallization depends upon the temperature, degree of supersaturation, surface area of the sucrose crystals, and the nature and concentration of the non-sucrose constituents. All of these factors influence the viscosity which is the limiting physical property in mechanical handling and hence governs to a large extent the technology of the process.

As massecuites are cooled, the diminished rate of crystallization due to lowering of temperature is compensated for by the increased rate arising from the lower solubility. Viscosity increases so rapidly, however, that the practical limit to which the massecuite can be cooled is governed by the ability of crystallizer equipment to handle the material. The viscosity at this limit, however, is such that the sugar cannot be separated from molasses efficiently in the centrifugals. Since, normally, the molasses mother liquor is still supersaturated in the massecuite that has reached the minimum tem-

perature, the massecuite may be heated to the saturation temperature of the molasses for centrifuging without loss of sucrose by solution. As an alternative procedure, water may be added to dilute the molasses to the saturation level. Both procedures reduce the viscosity so that separation of molasses from crystal becomes more effective.

Conditioning of massecuites in the crystallizer, accordingly, consists of controlled cooling from pan temperatures to a determined optimum temperature, followed by resolution of the supersaturation of the molasses. Exhausted molasses is rarely obtained because of the variability in composition and complexity of the multiple factors affecting crystallization. Proper equipment, instrument control and careful attention, however, will keep sucrose losses in molasses to a minimum.

2. Supersaturation

(a) *Coefficient of Supersaturation*

The degree of supersaturation of a molasses is indicated by the coefficient of supersaturation. This is the ratio of the amount of sucrose actually in solution at a given temperature to the amount dissolved in a saturated solution at the same temperature. The coefficient of supersaturation at a given temperature may be calculated from the formula

$$C_s = \frac{100 S}{WLC_1}$$

where

C_s = coefficient of supersaturation

S = % sucrose in mother liquor

W = % water in mother liquor

L = solubility of sucrose in water

C_1 = saturation coefficient, *i.e.*, ratio of solubility of sucrose in mother liquor to solubility of sucrose in pure water.

As pointed out by HARMAN¹⁴, if it is assumed that the saturation coefficient does not change with temperature, the equation reduces to

$$C_s = \frac{Lt_s}{Lt}$$

where

Lt_s = solubility of sucrose in water at the saturation temperature t_s of the mother liquor
 Lt = solubility of sucrose in water at temperature t .

Extending the simplification to impure sucrose solutions as found in natural syrups and molasses, HARMAN found only small variations. The error in the assumption that the saturation coefficient does not vary with temperature is generally in the order of 0.05. SAINT³⁷ found good agreement between the coefficients calculated by the two methods.

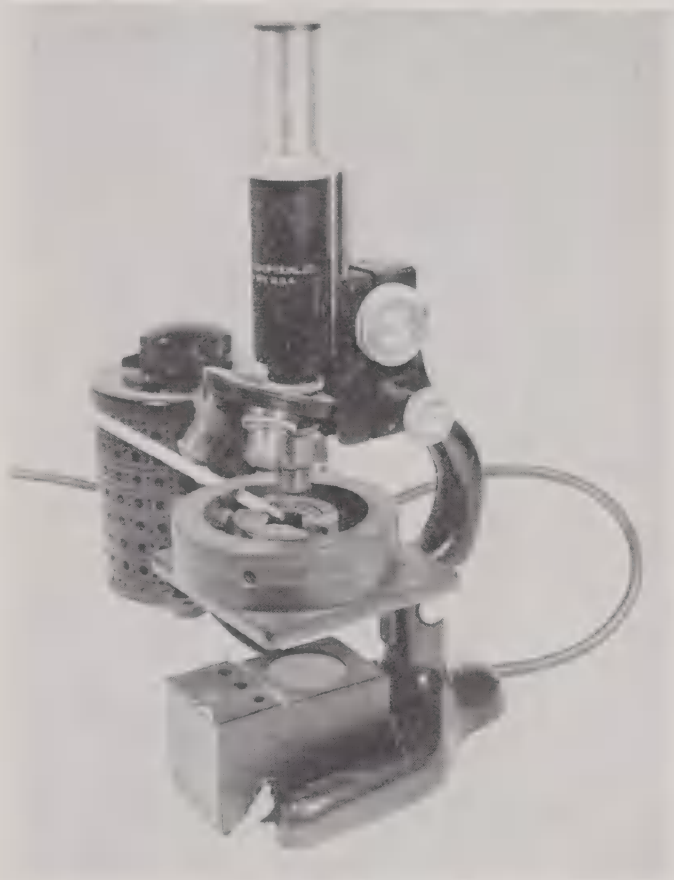


Fig. 13/1. Saturoscope, HSPA.

This simplified relationship makes possible the analytical determination of the supersaturation coefficient with ease, for it is only necessary to determine the saturation temperature. The saturation temperature thus becomes of basic importance in crystallizer work.

(b) *Saturation Temperature*

The saturation temperature of molasses in a massecuite is readily determined by use of an apparatus in which it is possible to observe the sucrose crystals under gradually increasing temperature. As the saturation temperature is

passed, the crystals begin to dissolve as evidenced by rounding of the sharp edges.

HARMAN¹⁴ described a saturation cell consisting of a flattened glass cell through which heated water is circulated and which is placed on the stage of a microscope for observation. SAINT³⁸ used a simple test-tube arrange-



Fig. 13/2. SUMA saturoscope.

ment, and KELLY²¹ a micro melting-point apparatus. The saturoscope developed in Hawaii²⁶ is shown in Fig. 13/1. A commercial instrument (SUMA) is shown in Fig. 13/2.

(c) *Use of Saturoscope*

The following directions are standard for use of the instrument for masseccuities:

1. Place a small quantity of the masseccuite between two micro cover-glasses. Squeeze them together gently, spreading out the masseccuite into

thin, uniform layer. Place the micro cover-glasses containing the sample in the center of the stage under the glass cover of the saturoscope.

2. Focus the microscope and adjust the saturoscope until a sharp edge or a broken section of a crystal with sharp points is brought into view.

3. Raise the temperature in the saturoscope about 0.5°C per minute by gradually increasing voltage until the crystal under observation starts to dissolve. The temperature at which the crystal begins to dissolve marks the temperature to which the material being examined can be heated without losing the purity of the mother liquor, and is the saturation temperature. Evidence that the saturation point has been reached can be indicated by various changes taking place in the appearance of portions of the crystal. If a sharp edge is chosen for observation, it becomes wavy or pitted. If a jagged edge on a broken portion of the crystal is being studied, the sharp points will disappear.

4. After the saturation temperature has been determined as outlined above, repeat the test on a second portion of the sample. This time increase the temperature rapidly to within about 3° of the saturation temperature found in the first test. Then increase the temperature very slowly until the crystal starts to dissolve. Record this as the saturation temperature.

The massecuite should not be spread between the micro cover-glasses so thin that there is not enough mother liquor in contact with the sugar crystals for them to start dissolving when the saturation temperature is reached. Spread the massecuite just thin enough so that a sharply outlined crystal may be selected.

(d) *Supersaturation in Crystallizer Practice*

Theoretically, the rate of crystallization is a resultant of the basic driving force toward crystallization and the opposing forces which impede crystallization. The driving force depends upon the degree of supersaturation. In crystallizer technology, therefore, optimum conditions are those in which the supersaturation is maintained as high as possible without entering a zone where new crystal nuclei are introduced. Massecuites are highly variable in this respect so that no generally applicable conditions can be set.

As cooling proceeds in the crystallizer, the rate of crystallization will decrease due to the temperature effect on velocity unless the degree of supersaturation is increased. SAINT³⁷ pointed out that the velocity of crystallization becomes very slow, even at as high a temperature as 68°C when the coefficient of supersaturation drops below 1.2. He found that

the following values represented approximately equal rates of crystallization:

Temperature °C	Coefficient of supersaturation
70	1.25
60	1.30
50	1.35
40	1.40

It is evident from these figures that there is no advantage in maintaining a constant temperature in the crystallizer for any long period of time for, as the sucrose crystallizes out, the supersaturation will drop and the rate of crystallization slow down. Proper crystallizer control in cooling requires establishing a rate sufficient to maintain supersaturation as high as practicable. In practice the supersaturation coefficients of low grade massecuites as dropped from the vacuum pan usually lie in the range of 1.10 to 1.25^{27, 28, 39}. Little change in these figures is found in the crystallizer during normal operation, sucrose crystallizing out at a rate consistent with the decrease in solubility as the material is cooled.

Similar conclusions have been drawn from the results of investigations on low grade beet massecuites. MCGINNIS, MOORE and ALSTON³⁰ reported that a minimum supersaturation of 1.50 was required at low temperature in the crystallizer to maintain an adequate rate of crystallization. Other investigators have confirmed these findings¹³.

3. Viscosity

The dominating factor in crystallizer technology is viscosity. This property sets, for the most part, the working condition limits within which processing in the crystallizer can take place. All other influencing factors must be controlled, therefore, within these limits. Since the viscosity varies extensively with the composition of the non-sucrose constituents, optimum operational procedures are attained by adjusting the principal variables, temperature and solids content, in order to reach desired viscosity ranges.

Viscosity relationships in sugar materials have been extensively studied. A survey of important papers in this field was made by MICHELI and DE GYULAY³². In this section the effect of viscosity on the more important factors affecting crystallizer operation will be discussed.

(a) *Rheology of Molasses and Masseccuites*

Viscosity is the resistance to flow of a liquid in moving over itself. The unit of viscosity is the poise. A liquid has a viscosity of one poise if a force of 1 dyne is necessary to cause two parallel surfaces 1 sq. cm in area and 1 cm

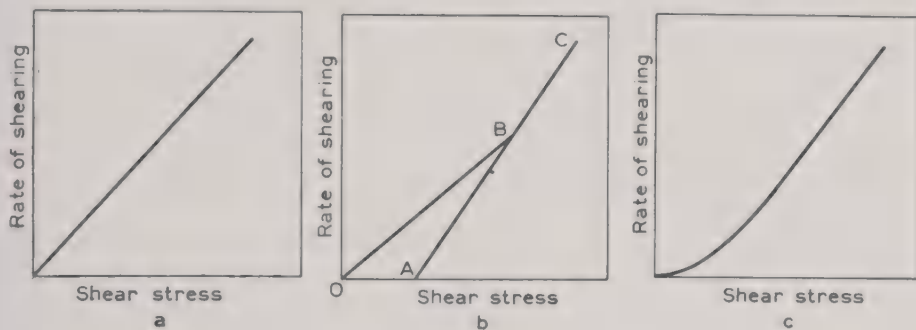


Fig. 13/3. Flow diagrams. a: ideal liquid; b: plastic flow; c: pseudo plastic flow. (From ADKINS¹).

part to slide past one another at a velocity of 1 cm/sec. It thus has the dimensions dyne-seconds per sq. cm.

For perfect liquids under the same conditions, the viscosity is constant, that is, the velocity is a straight-line function of the force applied. Many liquids, however, offer an initial resistance to flow and considerable force is necessary to overcome this. This is termed plastic flow. A third type of

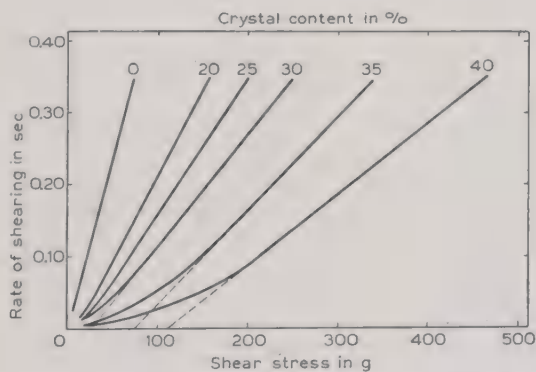


Fig. 13/4. Flow diagrams for masseccuites (From ADKINS¹).

liquid shows an intermediate behavior termed pseudo-plastic flow. These offer no initial resistance and flow starts immediately, but the velocity is low at first and gradually increases to give a constant viscosity. Diagrams for the three types of flow are shown in Figure 13/3 from ADKINS¹.

ADKINS found that molasses exhibits pseudo plastic flow to only a slight

degree. For practical purposes, therefore, it is only necessary to make one determination of rate of flow under a given force in order to establish the viscosity.

Masseccutes show pseudo plasticity to a much greater degree and true viscosity values can only be obtained from a series of rate-force determinations. Fig. 13/4 from ADKINS shows that the extent of the pseudo plasticity exhibited by masseccutes becomes greater at higher crystal content.

(b) *Effect of Nonsugar Constituents on Viscosity*

Physical conditions being constant, the viscosity of a molasses or masseccute depends largely upon the nature and concentration of the non-sucrose substances present. There is little quantitative information on the effect of various substances. Viscosities do vary widely, however, and relatively small quantities of some compounds have a pronounced effect. This is particularly true of organic compounds such as the gums, pectins, and other colloidal substances. Many inorganic salts likewise increase the viscosity⁴². As the composition is determined by the nature of the incoming juice, nothing can be done at the crystallizer station in this regard. It would be of great value nevertheless to know the individual and additive effects of the constituents in order to predict viscosity behavior.

(c) *Effect of Total Solids on Viscosity of Molasses*

The viscosity of molasses increases rapidly with increase in total solids content. Although various molasses may differ greatly in viscosity at a

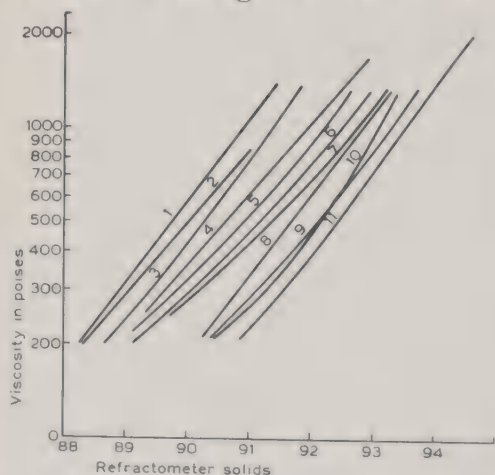


Fig. 13/5. Viscosity-refractometer solids curves of several Hawaiian molasses. Temperature 50° C.

given solids content, the rate of change with change in solids is similar. Fig. 13/5 shows the influence of solids as measured by refractometer on several Hawaiian molasses. The effect of temperature on average viscosity-refractometer solids curves for Hawaiian molasses is shown in Fig. 13/6.

The work of McCLEERY²⁷ on the relationship of total solids to viscosity in crystallizer studies is illustrated in Fig. 13/7. Here are plotted the values from 60 different masseccutes at three temperatures: 70° C, the time of

striking; 49°C , the minimum temperature in the crystallizer, and 57°C , the saturation temperature. The viscosity of these molasses approximately

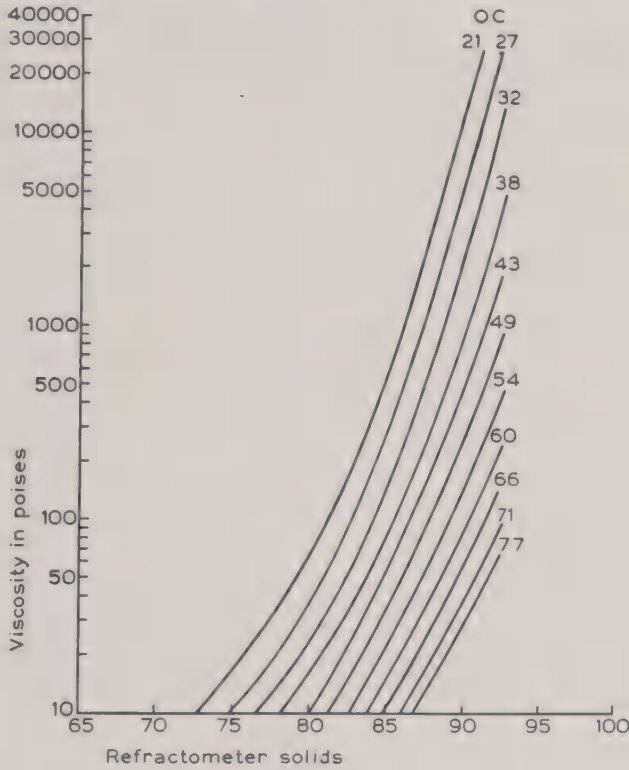


Fig. 13/6. Average viscosity-refractometer solids curves for Hawaiian molasses at various temperatures.

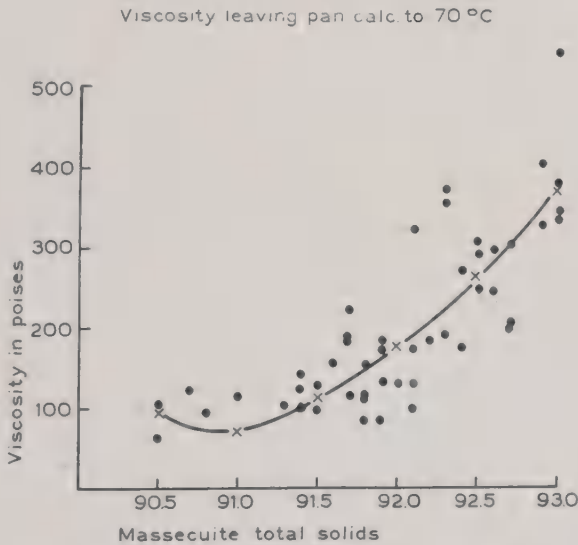


Fig. 13/7a. Massecuite total solids-molasses relationships for 60 different strikes at 70°C on leaving pan. (From McCLEERY²⁷).

doubles for each increase of 0.8% in total solids. The wide variation in individual molasses is illustrated, but also shown is the fact that if the

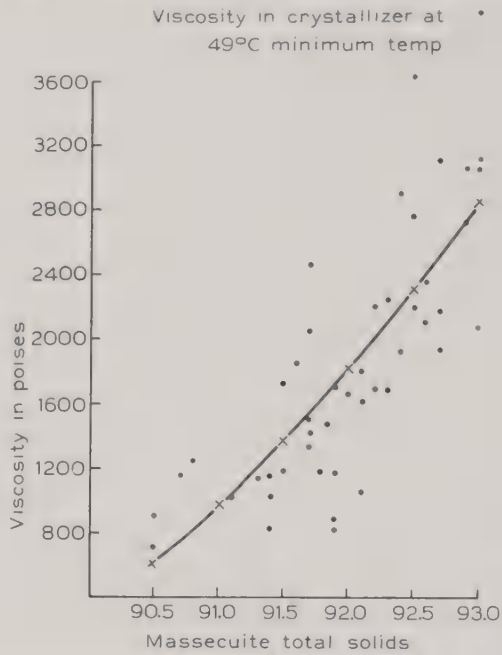


Fig. 13/7b. Massecuite total solids-molasses relationships for 60 different strikes at 49° C, minimum temperature in crystallizer. (From McCLEERY²⁷).

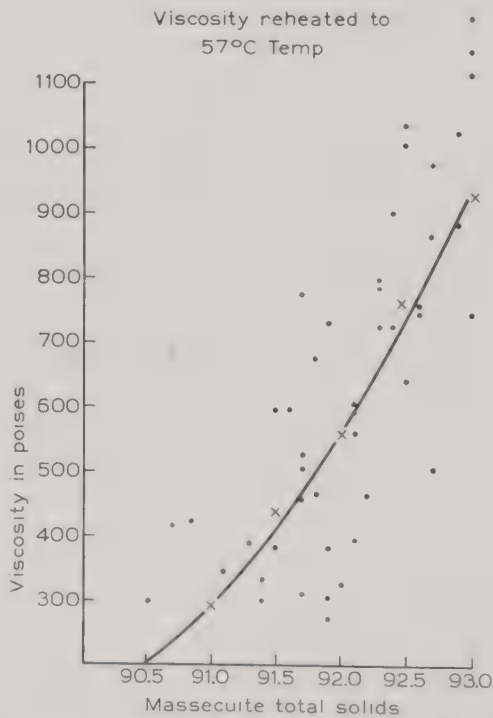


Fig. 13/7c. Massecuite total solids-molasses relationships for 60 different strikes at 57° C, saturation temperature. (From McCLEERY²⁷).

viscosity is high leaving the pan it will be high also during the crystallizer operation.

(d) *Effect of Temperature on Viscosity of Molasses*

The viscosity of molasses decreases sharply with rise in temperature. This is shown in the curves in Figs. 13/5 and 13/6. Although the slope of the temperature-viscosity curves for different molasses varies, it will be noted that all the curves are smooth and without any abrupt changes in slope. This holds true even in the range where the molasses passes from the unsaturated to the supersaturated state as pointed out by MICHELI and DE GYULAY³².

A most significant relationship between temperature and viscosity exists in that there is, for a saturated molasses at given purity, usually a temperature of minimum viscosity. The average value of this minimum was found by MCCLEERY^{27, 28}, MICHELI and DE GYULAY³² and KELLY²² to be close to 55° C. In Fig. 13/8 from BEHNE⁴ is shown a typical series of temperature viscosity curves for a molasses of the same purity at various total solids content.

The three broken lines represent constant saturation and supersaturation as indicated. Although the actual viscosities of individual molasses show a wide range in value, the minimum viscosity average occurs in the temperature range shown. This fact becomes a major consideration in the handling of massecuites in the crystallizer, and centrifugal and practical operation should be directed toward taking advantage of it.

(e) *Relation of Purity of Molasses to Viscosity*

Viscosity in itself apparently has no effect upon the minimum attainable purity of a molasses. This means that, as shown by VAN HOOK⁴⁶, artificially increasing the viscosity by use of a material such as a gum does not alter the exhaustibility. Viscosity does affect the workability of a massecuite, however, and due to the interrelationship between viscosity, total solids, composition, and temperature, there exists a definite correlation between viscosity and purity.

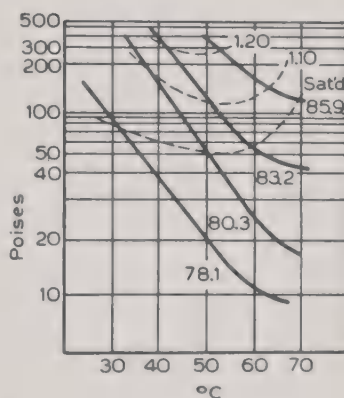


Fig. 13/8. Viscosity-temperature curves for molasses of same purity at different solids content. (From BEHNE⁴).

This was demonstrated by McCLEERY^{27, 28} to be extremely important at the saturation temperature. In Fig. 13/9 he shows gravity purity-viscosity curves for a typical molasses at various saturation temperatures. From these curves it is seen that at the same viscosity lower molasses purities are obtained at higher saturation temperatures up to 55° C. The vertical distances

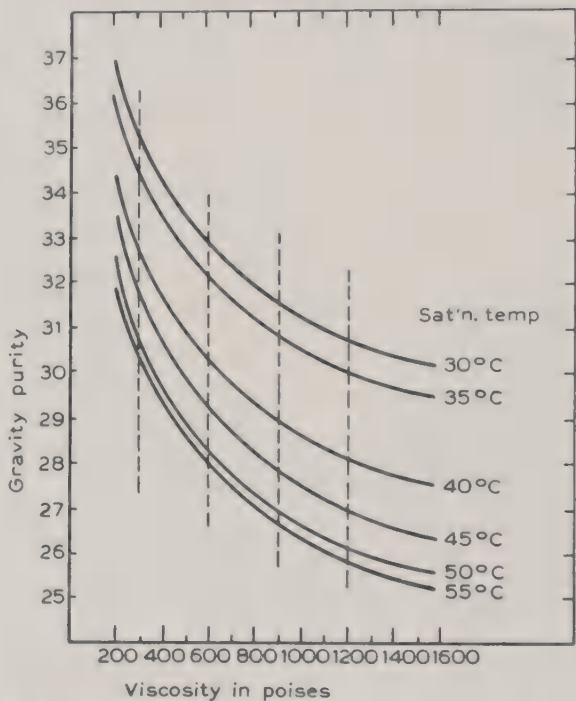


Fig. 13/9. Viscosity-gravity purity relationship at various saturation temperatures. (From McCLEERY²⁷).

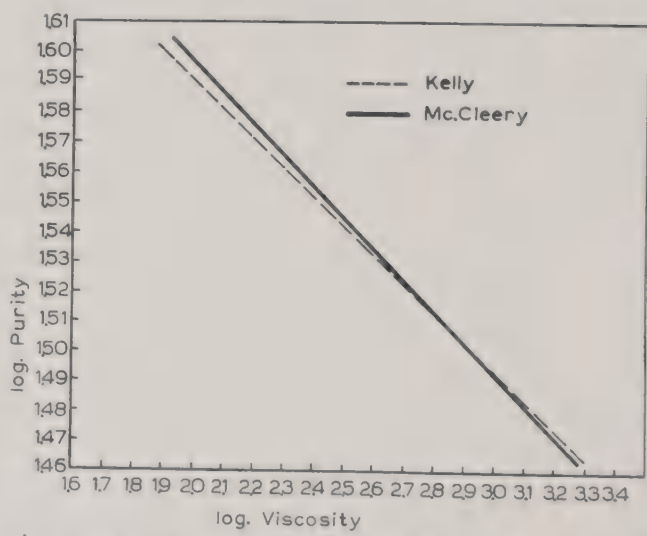


Fig. 13/10. Viscosity-true purity averages of KELLY and McCLEERY. Saturated molasses at 55° C. (From BEHNE⁴).

between the curves, representing purity changes, are the same at all viscosities.

KELLY²² found a similar correlation on a true purity basis and BEHNE⁴ showed that if McCLEERY's figures were changed to approximately the same basis the agreement between the two investigators would be extremely close. This is illustrated in Fig. 13/10.

Practical application of this principle can be made in crystallizer operation. Average optimum conditions required in massecuite handling are those necessary to produce molasses with a saturation temperature of approximately 55° C at the maximum viscosity that the massecuite can be handled in the crystallizer equipment. For a given molasses the higher the viscosity that can be reached, the lower the purity that can be achieved. This does not mean, of course, that more viscous molasses gives lower purities than less viscous ones. It means only that in every case it is advantageous from the purity standpoint to work with as high a viscosity as possible. Crystallizers should be designed to process high viscosity massecuites.

(f) *Relation of Reducing Substances-Ash Ratio to Viscosity*

The effects of salts in increasing the solubility, and reducing sugars in decreasing the solubility of sucrose in final molasses, have been firmly established. The relationship between viscosity and purity just discussed would indicate, therefore, that there should be some interdependence of

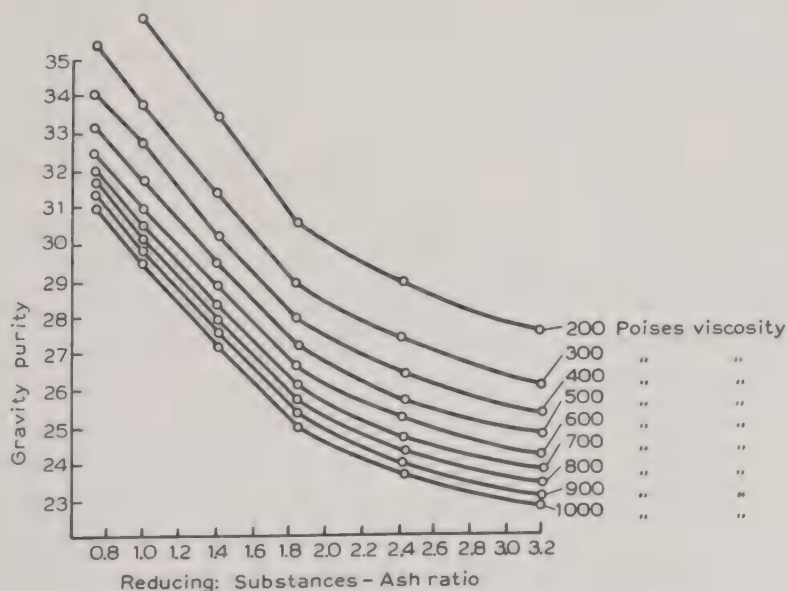


Fig. 13/11. Reducing substances-ash ratio vs. gravity purity at various molasses viscosities.

viscosity, purity, reducing sugars, and salts. That such is the case has been demonstrated in Hawaii where, for many years, factory control measures used in recovery of sugar from molasses are based upon the relationship of purity, reducing substance-ash ratio, and viscosity. At a definite viscosity the purity decreases as the reducing substance-ash ratio increases.

In Fig. 13/11 are typical curves for final molasses showing this relationship. From the analysis and exhaustibility studies of composite molasses from all producing areas of Hawaii, tables have been statistically calculated by use of which it is possible to estimate the purity of exhausted molasses³⁴. These tables are calculated to a standard viscosity of 600 poises and a saturation temperature of 50° C.

In the factory, having determined the analytical figure for the reducing substance-ash ratio, the operator has available at once an estimate of the purity of exhausted molasses at 600 poises and 50° C. Knowing the behavior of his material with respect to temperature and viscosity, and knowing likewise the capability of his equipment to handle various viscosities, he is enabled to judge the performance he is obtaining. Ash may be estimated conductimetrically so that the analytical procedures are rapid.

The usefulness and practical value of this method of estimating exhaustibility is indicated by the fact that it has a statistical correlation coefficient of 0.85. Deviations of actual purities from calculated at standard viscosity and saturation temperature are rarely more than 1.5 points³⁵. The method, of course, does not take into consideration the rate at which exhaustibility can be attained, but only the final exhausted purity. Since rates of crystallization are highly variable, the time required to reach exhaustion should be, but is not, taken into account in judging factory performance.

4. Crystal Content and Size

The rate of crystallization in the crystallizer will be greater the larger the surface area of sucrose crystals per unit volume. It is advantageous from this standpoint, therefore, to have small crystals and have them occupying as great a percentage of the massecuite volume as possible. Other factors, however, limit both the size and crystal content.

Crystals below a minimum size cannot be separated from the molasses in the centrifugal. Likewise a certain amount of molasses is necessary to keep the crystals apart and the massecuite fluid enough for handling, both in the crystallizer and in the centrifugals. It is very important that vacuum pan techniques be designed to give massecuites having the optimum crystal size and volume.

(a) *Crystal Content*

It has been shown in Fig. 13/4 that the viscosity increases as crystal content becomes greater. ADKINS¹ observed that up to a crystal content of 35–40% the log of viscosity is a straight-line function of the crystal content (see

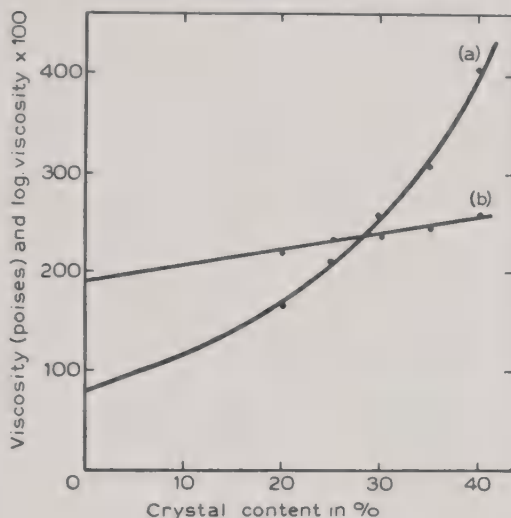


Fig. 13/12. Effect of crystal content on viscosity of massecuites. Curve *b* is logarithmic. (From ADKINS¹).

Fig. 13/12). There is such a marked increase in viscosity at crystal contents above 45% that normally this represents the upper working limit. The actual crystal content that is permissible with a given material depends upon the viscosity of the molasses; the lower the viscosity the higher the crystal content. As it is desirable to work with high molasses viscosities in order to reach lower purity, a compromise is necessary to arrive at a working crystal content. Most often this will be in the range of 35 to 40.

(b) *Crystal Size*

The necessity of having a large crystal surface in order to speed up rate of crystallization has been emphasized. This is also necessary if a rapid rate of cooling in the crystallizer is to be obtained, for, unless the crystal surface is adequate, supersaturation may rise to the range where spontaneous grain formation will occur. KELLY²² developed a useful formula expressing the relationship between crystal area per unit weight of molasses necessary to prevent spontaneous grain formation and purity of molasses at various degrees of supersaturation. We have the formula

$$SP^{1.4} = K$$

where

S = surface area in sq.ft./lb. of mother liquor

P = true purity of mother liquor

K = 2,000 at 1.1 supersaturation, 4,000 at 1.2 supersaturation, 8,000 at 1.3 supersaturation and 12,000 at 1.4 supersaturation.

If the surface area S falls below the value shown by the formula, spontaneous grain formation can be expected. The value of S may be estimated from the crystal size and crystal content of the massecuite using the formula (DRINNEN⁸):

$$S = \frac{19X}{l(100 - X)}$$

where

X = crystal content of massecuite

l = average length of side of crystal in mm.

For a massecuite of 30% crystal content, molasses purity of 40 and coefficient of supersaturation of 1.25, BEHNE⁴ shows that this calculates to an average length of side of 0.23 mm. If the size is larger at this content there is danger of new grain being introduced. If the crystal content could be increased, a larger crystal could be tolerated.

The effect of crystal size on viscosity has not been well established. ADKINS¹ reported W. G. DONE in a University of Queensland thesis as finding no effect of crystal size in the range 0.3–0.8 mm upon viscosity of massecuites. KELLY and MCANTEE²³, however, reported a substantial increase in viscosity over the same range. Their observations were made using a less suitable viscosimeter, however.

The limiting factor toward smaller crystal size is the ability of the centrifuge to remove the molasses. The smaller the crystal, the greater the time required to eliminate the molasses by centrifuging and hence the larger the centrifugal installation required. Of course, if the crystals become too small, centrifugal separation is impossible. A reasonable lower limit is close to 0.2 mm.

5. Crystal Movement

Circulation, which has been brought about by boiling and often by mechanical stirrers in the vacuum pan, must be continued to some extent in the crystallizer. It has been pointed out by VAN HOOK⁴⁷ that the energy requirements for crystal growth are considerably greater than those for diffusion and viscosity. This means that the rate of crystallization is determined by the speed at which sucrose is laid down in the crystal lattice rather than by

the speed of diffusion. Rate of stirring, therefore, will have little effect upon the rate of crystallization in the crystallizer, other factors being equal. Nevertheless, it is most important to maintain enough movement of the massecuite to prevent settling of the crystals by gravity and to maintain uniformity of distribution of the crystals throughout the massecuite. Although it is not possible to effect much movement of crystals relative to molasses on account of the high viscosity, it is possible by slowly moving stirrers to maintain good uniformity.

Aside from maintaining this distribution of crystals, the main purpose of stirring is to effect rapid and uniform heat transfer. This is necessary in order to maintain optimum conditions of temperature and supersaturation. Engineering design of crystallizers has thus been directed toward equipment which will give maximum efficiency in heat transfer. This, of necessity, requires movement of massecuite as has been discussed in the previous chapter.

6. Cooling

Cooling of massecuites in the crystallizer has been covered from the standpoint of heat transfer in a previous chapter. As stated before, the purpose of cooling is to continue sucrose crystallization after isothermal crystallization has been carried to the practicable limit in the vacuum pan. This is done by taking advantage of the lower solubility of sucrose at lower temperature.

Massecuites are dropped from the pan at temperatures in the range 65–70° C. The attainment of additional crystallization then requires decreasing the temperature to the minimum at which the material can be mechanically stirred, viscosity being the limiting factor, and allowing crystallization to take place until the molasses will have a saturation temperature approximating that of centrifuging. Under optimum conditions this is approximately 55° C. The minimum temperature to which the massecuite may be lowered in the crystallizer depends upon the viscosity, but most often lies between 45 and 50° C.

The optimum rate of cooling is that in which the supersaturation is kept as high as possible, in order to maintain the highest possible rate of crystallization, without the formation of new grain. Engineering design limitations are such that the problem of reducing temperature uniformly throughout the massecuite becomes the major one. With uniform cooling, too rapid cooling is rarely troublesome. Crystallizer design, therefore, becomes a matter of obtaining maximum heat transfer area per unit volume with optimum movement of the material.

The literature in crystallizer design and performance is voluminous^{2, 3, 6, 9, 10, 11, 15, 16, 17, 18, 19, 24, 25, 27, 29, 36, 41, 43, 44, 48, 49, 50}. Design has advanced from a simple air-cooled tank, through water-jacketed, and fixed coil units, to contemporary types, most of which have rotating parts through which water can be circulated. Examples of types most widely

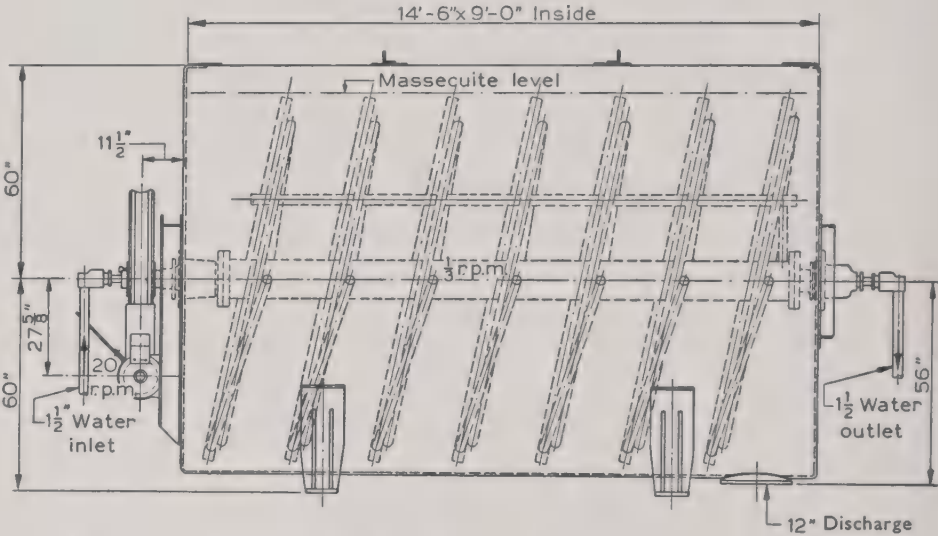


Fig. 13/13. Revolving coil crystallizer, HONOLULU IRON WORKS type.

used are the LAFEUILLE rotating crystallizer, BLANCHARD with hollow stub arms in various forms of modification, the WERKSPOOR with discs, and the HONOLULU IRON WORKS with rotating coils (Fig. 13/13).

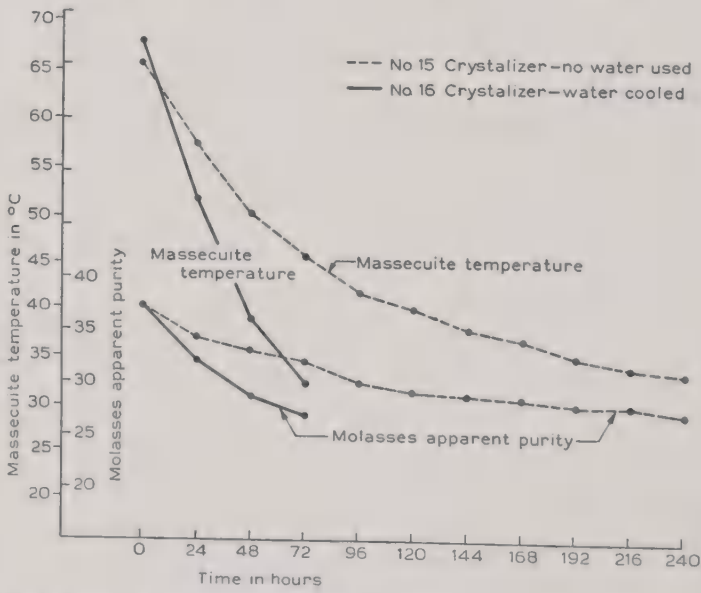


Fig. 13/14. Effect of water cooling in crystallizer on temperature and purity.

Crystallizers equipped with liquid cooling units permit much more rapid reduction in temperature than those that are air cooled. This is illustrated in Fig. 13/14. The resulting crystallization rate with more efficient cooling is shown by the early attainment of lower purity values. McCLEERY²⁷ has discussed the variables of water rate, speed of rotation of coils, and surface

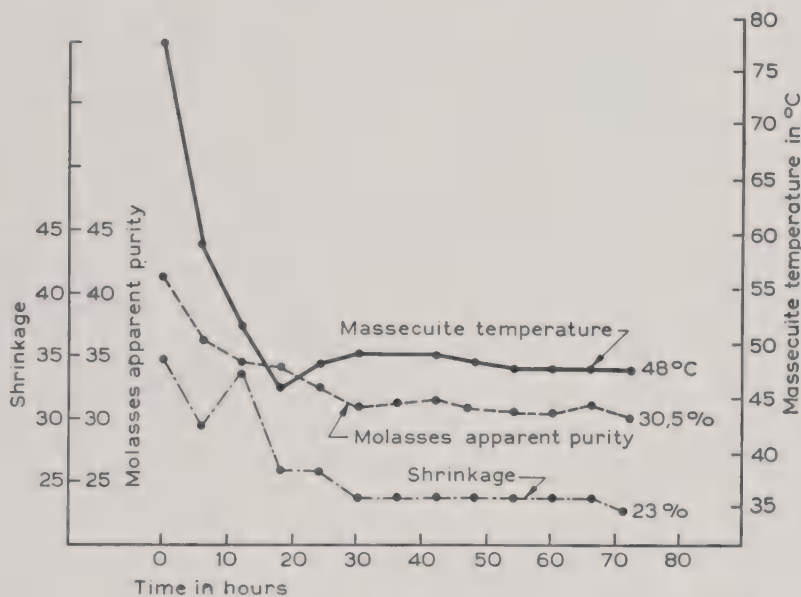


Fig. 13/15. Crystallizer cooling curve in HONOLULU IRON WORKS type crystallizer.

area of coils in relation to time of cooling. With a cooling area of 0.6 sq. ft./cu. ft. volume, in a Honolulu Iron Works type crystallizer, massecuites can be cooled from 70 to 50° C in seven hours without danger of introducing new grain.

A cooling curve from a massecuite in a crystallizer of this type is shown in Fig. 13/15. The massecuite is cooled relatively rapidly to the desired minimum temperature. It can then be held at this minimum for a time sufficient to reach a chosen coefficient of supersaturation as measured by the saturation temperature; this is done by circulating water through the coils at a temperature approximately 1° C above the desired minimum. This curve which is typical of heavy boiled massecuites shows that the crystallization rate becomes very slow after 30 hours so that little is gained from a longer holding time in this type of crystallizer.

In general, it can be stated that cooling in the crystallizer should be as rapid as possible, the temperature to which the massecuite is cooled as low as viscosity will permit, and the time during which the minimum temperature is maintained is governed by the coefficient of supersaturation.

7. Reheating and Diluting

When the degree of supersaturation has diminished to the point where the rate of crystallization is too slow to have any practical effect, the massecuite is ready for centrifuging. The efficiency of this step will be improved if the viscosity is lowered by reducing the supersaturation. This can be accomplished by reheating to the saturation temperature, diluting with water to the saturation point, or a combination of both.

The question as to whether the massecuite should be heated or diluted must be considered from both the theoretical and practical standpoints. Theoretically, the procedure adopted should be the one that gives the lowest viscosity molasses. Here again there is a variation depending upon the composition of the molasses. In general, the temperature-viscosity-solids relationship is such that for lower solids molasses lower viscosities are obtained by reheating to the saturation temperature, whereas for higher

solids molasses a lower viscosity will be obtained by dilution. This is illustrated in Fig. 13/8 which has been cited previously. These curves show also that at the temperature of minimum viscosity, about 55° C, the advantage lies in reheating. The results of MITCHELL and BEHNE³³ as shown in Fig. 13/16 demonstrate the same favorable effect of dilution on viscosity at higher solids (above 85 total solids undiluted), an advantage which disappears with lower solids content.

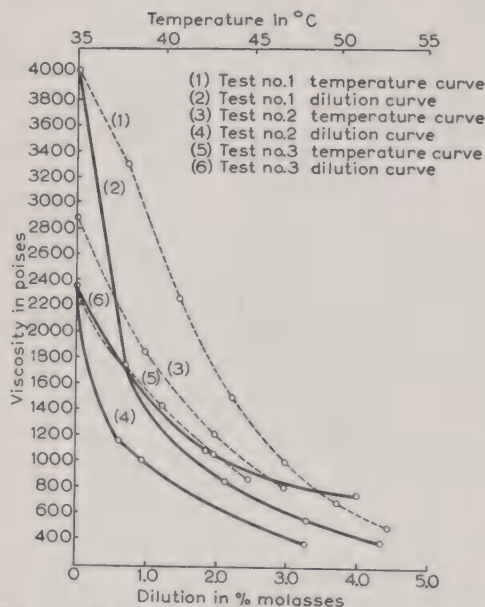


Fig. 13/16. A comparison of the effects of diluting with reheating on viscosity. Total solids before diluting: Test 1, 85.33; Test 2, 85.25; Test 3, 84.72. (From MITCHELL and BEHNE³³).

temperature alone. Dilution will then be required on occasion only as an emergency measure.

Reheating can be accomplished by circulating warm water through the cooling units of the crystallizer. This water should not be more than 2° C above the saturation temperature if local overheating is to be prevented.

On reaching the saturation temperature the massecuite is ready for centrifuging. In order to shorten the total time in the crystallizer, some of the heating may be done in a separate heater or with heating coils in the mixer supplying the centrifugals.

8. Conductivity Control

Indication and control of supersaturation and exhaustion in the crystallizer by conductance methods have been extensively investigated in the beet industry^{13, 31, 40}. Some work has also been done on cane massecuites^{7, 45}.

The electrical conductance of a massecuite increases as supersaturation decreases. As conductance varies directly with temperature, control of cooling in maintaining a definite degree of supersaturation is possible by means of a combination of conductance and temperature measurements. The conductance, however, is greatly dependent upon composition of the massecuite as well as upon the amount of crystals present²³. The method, therefore, must be standardized for a fixed type of composition as well as crystal content before it is a useful control procedure. Nevertheless, the ease with which conductance measurements can be made makes thorough investigation of the applicability of this type of control in a given case worthy of careful consideration.

9. Molasses Exhaustibility

Although the question of molasses exhaustibility is covered thoroughly in Chapter 14, it has such an important bearing upon crystallizer operation that some discussion should be made at this time.

Since the purpose of crystallizer work is to crystallize out as much sucrose as possible from the final molasses, the exhaustibility is always a determining factor in the results obtained. This exhaustibility, or minimum attainable purity, is highly variable. Many of the factors affecting this value remain unknown. It is important nevertheless to keep in mind the generalizations which may be drawn from available evidence.

As related earlier, there is an extremely important inverse relationship between the total solids content of molasses and the minimum attainable purity. This means simply that the less water present, the less sucrose that can remain dissolved. As viscosity varies directly with solids, it follows that the higher the viscosity, the lower the theoretically attainable purity of molasses. Also pointed out was statistical correlation between the purity at exhaustion and the reducing substance-ash ratio at a given viscosity.

Although further investigation is necessary to pinpoint the effect of the individual constituents, this interrelation forms a valuable basis for setting up operational procedures and controls.

The theoretically attainable purity is determined by the amount and nature of the non-sucrose constituents present. The practicably attainable purity is determined also by the effect of these constituents on such factors as viscosity and crystallization rate. It follows that the purity of molasses attained at a given time is not necessarily an indicator of efficiency of the pan and crystallizer operations. Viscosity of various molasses at the same temperature and solids content may vary tenfold. Rates of crystallization at the same temperature and degree of supersaturation will differ very widely. Equipment capacity and design play a very important role. Only by a study of all factors involved can the decision be made as to relative efficiencies from strike to strike, factory to factory, or area to area.

10. Summary and Conclusions

The evidence presented in this chapter indicates that the maximum yield of sucrose can be obtained by application of the following practices:

1. Boil massecuites entering the crystallizer to such a total solids content that the viscosity is not too great for the material to be handled successfully (*a*) in the crystallizer when cooled to the optimum temperature and (*b*) in the centrifugal when reheated to the saturation temperature.
2. Control crystal content, size, and uniformity so that (*a*) surface area of crystal is adequate for optimum crystallization rate, (*b*) crystal content is not larger than the maximum at which the massecuite can be handled (about 45%) and (*c*) crystals are of sufficient size and uniformity to permit efficient separation from molasses in the centrifugal.
3. Cool the massecuites as rapidly as possible in the crystallizer to obtain a degree of supersaturation sufficient to maintain crystallization velocity without danger of spontaneous introduction of new crystal nuclei.
4. Lower the massecuite to the minimum temperature at which the crystallizer equipment can process it, as determined by viscosity.
5. Maintain this minimum temperature until the saturation temperature approximates 55° C.
6. Reheat the massecuite to the saturation temperature as rapidly as uniformity of heating will permit.

The massecuite is then ready for centrifuging and it remains to set up procedures by which these general conditions can be maintained on a practicable basis. No closely defined specification can be set up which will

be widely applicable due to the uncontrollable variations in composition. Each factory, therefore, must investigate completely its own situation with regards to the effect of the variables, temperature, supersaturation, and viscosity.

BEHNE⁴ has summed up a procedure illustrated by Fig. 13/17 as follows.

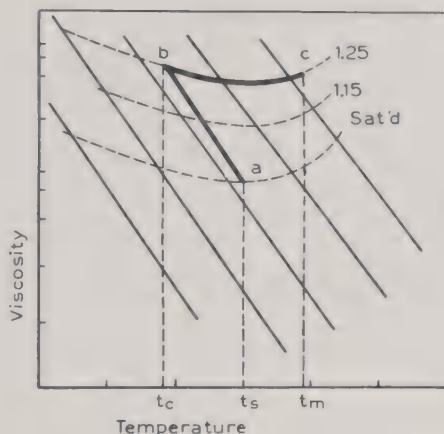


Fig. 13/17. Reheating diagram showing minimum viscosity. Point *c* is on plane above graph and line *cb* connects the two planes. (From BEHNE⁴)

'In this illustration the minimum viscosity is at *a* or saturation temperature t_s which is usually about 55°C . . . a maximum degree of supersaturation of 1.25 has been assumed, *i.e.*, the strike is dropped to the crystallizer at this value. Repeated investigations have shown that the degree of supersaturation does not vary greatly during crystallization. Consequently, on the completion of the crystallizer work, the supersaturation will still be in the vicinity of 1.25. If, therefore, a line be drawn through the saturation point *a* parallel to the viscosity lines, it will cut the 1.25 supersaturation line at a temperature of t_c $^\circ\text{C}$ (*b*). This is the value to which the massecuite should be cooled before reheating to t_s $^\circ\text{C}$ is commenced. The condition in which the massecuite is dropped is determined by following the 1.25 saturation line round to the temperature t_m of the pan at the finish of the heavying up. The actual temperature will depend upon several factors, *e.g.*, the vacuum available, but should be in the vicinity of that corresponding to the minimum viscosity. Published data in regard to temperature corresponding to the minimum viscosity for 1.25 supersaturation for the purities in the 55–60 range are meagre, but the indication is that the temperature is usually high – in the vicinity of 70°C .

'The dry substance of the molasses is determined once the solubility coefficient and final molasses purity are fixed, whilst in addition the crystal content of the massecuite at fugalling fixes the dry substance and purity of the massecuite. The corresponding values of the conductivity at which the massecuite is to be dropped to conform to these requirements would have to be determined experimentally.

'The most satisfactory size of grain may be determined by the use of KELLY's²² relationship, $SP^{1.4} = K$, where, for 1.25 supersaturation $K = 6,000$, *S* is the surface area of the crystals in sq.ft./lb. of mother liquor of purity *P*. This is used in con-

junction with the surface weight ratio established by DRINNEN⁸. For a crystal content of x %, the size of crystal in mm is given by $\frac{19x}{S(100 - x)}$. When $x = 30$,

this value becomes $\frac{8}{S}$ approx.

'Once, however, the approximate procedure has been established, occasional checking should enable a reasonably tight control to be maintained.'

Referring again to Fig. 13/9, the desirability of reaching a saturation temperature close to 55° C is obvious. Likewise, lower molasses purities will be reached at higher viscosities. The molasses purity that will be obtained, therefore, is limited by equipment design. Good crystallizer technology requires close attention to saturation temperatures, viscosity relationships and temperatures. A prerequisite to this is pan technology which will give massecuites of proper total solids, crystal size and crystal content to the crystallizer station, for inadequate pan work cannot be corrected in the crystallizer.

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CHAPTER 14

MAXIMUM RECOVERY OF CRYSTALLISED SUCROSE FROM LOW GRADE BOILINGS

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1. Introduction

The inability of sugar manufacturers to recover in the crystallised state all the sucrose present in cane and beet juice has created the molasses problem. The loss of sucrose suffered by cane sugar factories in final or exhausted molasses is considerable, *viz.* 5–13% of the amount of sucrose present in mixed juice.

The importance of this loss and its variability have prompted generations of scientists to study its nature in attempts to reduce its volume.

The general principle underlying sugar manufacture is to remove water by evaporation from the raw material fed into the boiling house until sucrose starts crystallising, and to continue such removal, although intermittently interrupted in order to remove sucrose crystals, until it has to be concluded for the practical reason that a further removal would make the material too stiff to be worked by the factory plant. It then still contains a fair proportion of water, and since sucrose is soluble in water, a fair amount of sucrose, which is bound to be lost to the sugar manufacturer and is discharged from the factory as final molasses.

Hence the amount of sucrose lost depends on (a) the amount of water present in final molasses, and (b) the ratio of sucrose to water.

Often a small quantity of very fine sucrose crystals which slipped through the openings of the centrifugal gauze is also present.

Apart from these fine crystals final molasses is a liquid mixture of sucrose, water and an unknown number of certain other substances usually known as nonsucrose ingredients, or collectively as nonsucrose. Such a mixture is said to be a saturated solution if in equilibrium with the solid phase of one of the solutes. Molasses is said to be saturated if in equilibrium with solid

sucrose, and the ratio of sucrose to water in saturated molasses is usually called the solubility of sucrose in molasses.

The solubility varies with the temperature, and is also affected by the amount and nature of the other substances present. If less sucrose is present than corresponds to its solubility under the given conditions, molasses is said to be undersaturated, if more sucrose is present supersaturated.

The amount of sucrose present above the amount corresponding to the solubility is theoretically available for crystallisation. The rate at which the supersaturated sucrose will crystallise depends on certain factors which are discussed elsewhere in this book. Amongst them the amount and nature of the nonsucrose ingredients also present are of predominant importance. The rate of crystallisation of the sucrose held by the molasses in supersaturation is generally slow when compared with the rate of crystallisation from pure supersaturated solutions of sucrose and can be almost zero in some cases.

Hence at the end of the crystallisation period final molasses is nearly always supersaturated, particularly so when the temperature during crystallisation has dropped to below 40°C . The ratio sucrose: water in ordinary final molasses is thus generally not indicative of the solubility of sucrose in this particular system and in order to study the factors affecting the solubility extreme care has to be taken that equilibrium has been attained.

A considerable part of all investigations carried out in connection with the molasses problem are concerned with the solubility of the sucrose in the water present in the molasses and the factors affecting this ratio. Other investigations deal with the effect of the removal of water from molasses on certain properties of this material, in particular its viscosity, for although the effect of viscosity on the recovery of crystallised sucrose from sugar liquors is not known in detail, the importance of the viscosity as the main factor limiting concentration is generally recognised.

For a proper appreciation of the present conceptions in regard to the molasses problem an insight into their historical developments is indispensable.

The earliest investigations dealt with beet molasses, but in 1892 PRINSEN GEERLIGS, in Java, published a paper¹ on melassegenic substances which is one of the oldest endeavours in the cane sugar industry to increase our knowledge of the formation of final molasses by a systematical study of the problem. Attention in those days was mainly focussed on the difference between the losses of sucrose in beet and cane molasses for which an explanation had to be found.

The first fact requiring explanation concerned the sucrose solubility in

beet molasses which was higher than in a pure aqueous solution of sucrose of the same temperature whilst the sucrose solubility in cane molasses was lower. This fact is illustrated by the following data.

	grams per 100 grams of water
Solubility of sucrose in aqueous solution at 20° C	203.9 (ref. ²)
Average sucrose content of German beet molasses per 100 parts of water	243 (ref. ³)
Average sucrose solubility of three selected Java molasses whose saturation temperature was 50° C	191 (ref. ⁴)
Solubility of sucrose in aqueous solution at 50° C	260.4 (ref. ²)

In 1895 PRINSEN GEERLIGS offered an explanation⁵ which, elaborating on an earlier assumption by GUNNING⁶, dominated all work on exhaustion of final molasses for a considerable period of time. PRINSEN GEERLIGS assumed that many nonsucrose components, amongst which organic alkali-salts excelled, could combine with sucrose and water into easily soluble, syrupy compounds. In this way water in molasses could dissolve more sucrose than corresponds with the normal solubility. The assumption of the hydrated sucrose-salt compounds readily explained the higher sucrose solubility of beet molasses.

If, however, in addition to salts and sucrose, glucose (see p. 517) was present, the conditions changed. For due to its aldehyde-group glucose was assumed by PRINSEN GEERLIGS to form hydrated glucose-salt compounds more easily than sucrose. Hence part of the water was withdrawn by such compounds and no longer available either to dissolve sucrose, or to form sucrose-salt compounds if salt was present in excess of the amount needed for the glucose-salt compounds. In this way PRINSEN GEERLIGS explained the lower solubility of sucrose in cane molasses.

It is interesting to note that PRINSEN GEERLIGS has never been capable of proving the existence in final molasses of hydrated sucrose-salt compounds. Moreover his experiments showing that glucose does not affect the solubility of sucrose in water – on which his assumptions were partly based – were later proven to have been misleading, for reducing sugars actually lower the solubility.

The assumption of hydrated sugar-salt compounds has probably not been very conducive to further serious study of the molasses problem. One simply had to accept their existence which would thwart all attempts to reduce the purity of final molasses.

However in 1915 VAN DER LINDEN⁷ published papers in which the molasses problem was discussed on the basis of phase rule considerations.

Molasses being a very complex system, and solubility data hardly being available at that time, VAN DER LINDEN's expositions were semi-quantitative only. They have, however, contributed considerably to a better understanding of the nature of molasses, and not less important, have prompted many systematical investigations into equilibrium conditions in systems consisting of the main components of final molasses.

Generally speaking the outcome of all this work was that we have to see final molasses simply as a (super-)saturated solution of sucrose. Further crystallisation of sucrose by further removal of water is mainly limited by the decreased workability of the material. The realisation of this fact has drawn the attention to the factors controlling the viscosity of molasses, and the study of these factors has revealed many interesting relationships.

The factors controlling the solubility of sucrose in molasses, in particular the effect of certain groups of nonsucrose components, have also been subjects of investigation. In addition to exhaustibility tests aimed at finding relationships between purity and nonsucrose composition, statistical studies have been made which have led to the development of formulae with which a target purity can be calculated from the ratios between the amounts of certain nonsucrose components present.

The molasses problem has not yet been solved in such a way that all loss of sucrose is obviated, but a much better understanding of the factors limiting further crystallisation has been achieved. And when we compare the loss of sucrose in final molasses in 1895 with the present loss an appreciable reduction is evident.

2. Phase Rule Considerations

For the sake of simplicity, molasses will be considered as a ternary system consisting of sucrose (s), water (w) and a third component, nonsucrose (n). Two alternatives have to be considered:

- (a) The components do not form compounds.
- (b) The components do form compounds.

PRINSEN GEERLIGS' hydrated sugar-salt compounds fall into the latter category, and will be discussed after the more simple system (a) has been studied. This system can conveniently be represented by a diagram as shown in Fig. 14/1⁷.

The corners of triangle smw represent the three components of the system; on the vertical axis the temperature is measured. The melting points of the components are given by S , W and N , the binary eutectics are E_1 , E_2 and E_3 .

On the face $SsnW$ we find the solubility curves of the binary system sucrose-water. The melting point S of s is higher than W of w , hence the eutectic E_2 is probably nearer to W than to S , *i.e.* the eutectic mixture may contain more w than s .

We do not know whether the melting point of n is higher or lower than that of s . Therefore both possibilities will be considered. The case of n having a high melting point N is illustrated in Fig. 14/1; Fig. 14/2 shows the case of a relatively low melting point, here called I .

The curves indicating the effect of the presence of a third component on the binary eutectics E_1 , E_2 and E_3 meet at E , the ternary eutectic (Fig. 14/1).

Of main interest is the face SE_1EE_2 , the so-called sucrose solubility surface.

Assume P represents a homogeneous mixture of s , n and w of a suitable composition. If such a mixture is cooled, point B (Fig. 14/1) on the sucrose surface SE_1EE_2 will be reached and thus saturation in respect of sucrose. On further cooling sucrose will crystallise and the composition of the liquid phase will be represented by points moving along line BC as more solid sucrose separates. At C the intersection with eutectic curve E_1E is reached where the mixture also becomes supersaturated in respect of n . Continued cooling will result in one of three things happening:

- Both solutes will crystallise either as individual entities, as a solid solution, or as a double compound.
- One of the solutes will crystallise leaving the other in a metastable state of supersaturation.
- The solutes will interfere with each other in the solution in such a way that neither will crystallise⁸.

LEOPOLD JESSER⁹ who was the first to apply phase rule considerations to beet molasses, assumed that alternative (c) prevailed. He regarded mo-

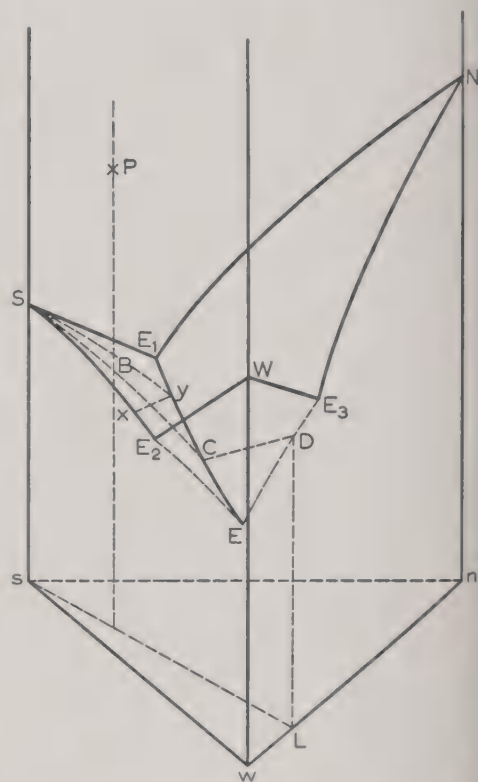


Fig. 14/1. Phase diagram showing equilibrium conditions in a ternary system consisting of n , s and w , n having a high melting point. (VAN DER LINDEN)

be cooled to temperatures below 30°C and sucrose would have to crystallise.

Not only will the eutectic line E_1E be at a lower level for a lower melting point of the third component, but E_1 will be shifted further from S , and line xy in Fig. 14/2 will probably represent molasses of lower purity than line E_1y in Fig. 14/1.

Apparently the lower the melting point of n the lower the purity of final molasses which is saturated at 30°C . This relationship might explain why beet molasses generally has a higher purity than cane molasses, the melting point of n in beet molasses (mainly salts) being higher than the melting point I of cane molasses, where i is mainly a mixture of salts and reducing substances.

If JESSER was incorrect in assuming that alternative (c) prevails, either both solutes crystallise (i) if E_1E is reached, or only one, leaving the other in a metastable state of supersaturation (ii). In the former case crystallised sucrose will be obtained, but very impure and of little commercial value. Hence further cooling after the eutectic line E_1E has been attained serves a useful purpose only if alternative (ii) prevails. In that case final molasses

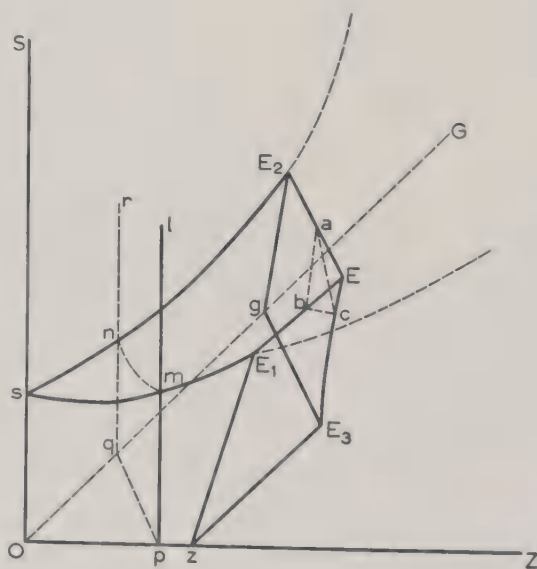


Fig. 14/3. Equilibrium conditions in a quaternary system consisting of S (sucrose), G (glucose) and Z (salt) in water at a fixed temperature. (VAN DER LINDEN)

would be a metastable saturated solution of sucrose, and further crystallisation is in principle possible by further cooling.

In the above the effect of the nature of n on equilibrium conditions has already been touched upon. A better insight can be gained by following

VAN DER LINDEN in his further studies of a quaternary system consisting of sucrose, water, glucose* and salts. To represent such a system VAN DER LINDEN used a space model as shown in Fig. 14/3.

This model shows the conditions for one temperature only, *e.g.* 30° C. The quantities of *S* (sucrose), *G* (hexose) and *Z* (salt) set off along the perpendicular axes are those present per 100 grams of water.

In plane *SOZ* we find the solubility conditions of sucrose and salt in water, in plane *SOG* of sucrose and hexose, in plane *GOZ* of hexose and salt. In E_1 , E_2 and E_3 the liquid phase is in equilibrium with two solids, and by addition of the third solid eutectic curves are followed. These curves meet at *E*, the Invariant Point, representing the condition of equilibrium of the liquid phase with the three solids.

Each point of the volume bordered by the planes *SOG*, *GOZ* and *SOZ* and the surfaces EE_1sE_3 , EE_2sE_3 and EE_1sE_2 represent an undersaturated liquid, each point outside this volume a liquid phase saturated with at least one solid.

For our purpose, the surface sE_1EE_2 representing the conditions under which sucrose separates from the liquid phase, is the most important. The points to the left of E_2EE_1 represent stable saturated solutions, those to the right metastable saturated solutions. Every massecuite is represented by a point above the sucrose surface and the intersection of the vertical through this point with the surface gives the saturated molasses corresponding to this massecuite. Whether this point is part of the stable or the metastable section of the surface depends on the water content of the massecuite. The shape of the surface illustrates the properties of the massecuite and molasses. The curve sE_2 shows the effect of hexose on the solubility of sucrose, the curve sE_1 the effect of salt. Most salts first lower and at higher concentrations increase the solubility of sucrose in water. And since hexose decreases the solubility, points on the surface near to sE_2 will generally be lower than the corresponding points near to sE_1 .

Further, since the addition of hexose to a salt-containing sucrose solution usually results in crystallisation of sucrose, the sucrose surface starting from points on sE_1 and proceeding in the direction of *OG* will initially show a depression. The surface will also show a depression starting from points on sE_2 proceeding parallel to *OZ*, for PRINSEN GEERLIGS has already shown that the addition of some salts to a hexose containing saturated

* Some authors use the word glucose for the variable mixture of dextrose and levulose occurring in sugar cane products. This custom should not be encouraged. If the word reducing sugars is too cumbersome, hexose would be much better. In the following, the word hexose will be used where expedient.

solution of sucrose initially brings about crystallisation of the latter substance.

Since the sucrose surface tends to rise in the metastable section, the depression is of limited extension. The complete situation can best be shown by a family of intersections of the sucrose surface with vertical planes

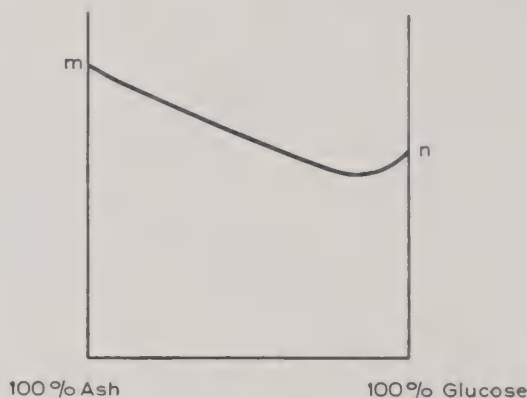


Fig. 14/4. Intersection of the sucrose surface of Fig. 14/3 with a vertical plane perpendicular to GOZ and intersecting OG and OZ at angles of 45° . (VAN DER LINDEN)

perpendicular to GOZ and intersecting OG and OZ at angles of 45° . Of these planes $rqpl$ is shown in Fig. 14/3 and separately in Fig. 14/4. In all points of this plane the quantity of nonsucrose (salt + hexose) per 100 parts of water is the same, *viz.* p . The quantity of sucrose per 100 parts of water at $t^\circ \text{C}$ is m if nonsucrose is salt, and n if nonsucrose is hexose.

If $pqrl$ is situated near the centre of the depression of the sucrose surface

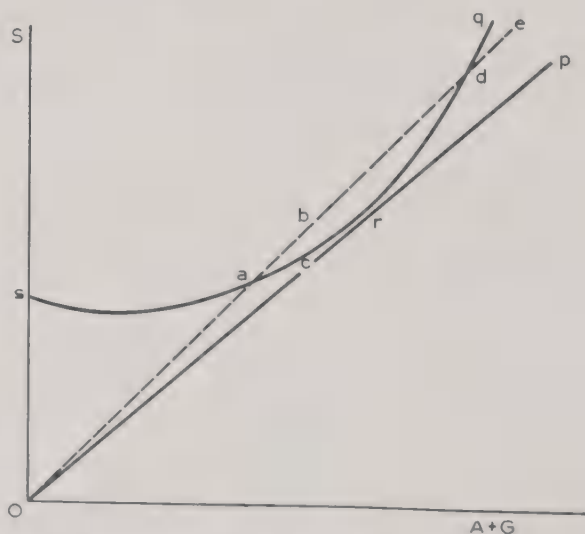


Fig. 14/5. Intersection of the sucrose surface of Fig. 14/3 with a vertical plane through OS . (VAN DER LINDEN)

the curve mn will show a minimum near to n , *i.e.* the sucrose solubility is at a minimum for a certain ratio of hexose to salt. Generally speaking the purity of the liquid phase will be lower when nonsucrose is mainly hexose and higher when mainly ash.

Also of interest is the family of planes through OS , *i.e.* those perpendicular to GOZ , and their intersections with the sucrose surface. Extremes of such intersections are sE_1 and sE_2 . Each other plane represents a definite ratio of hexose to salt.

Fig. 14/5 shows such a plane, srq being the intersection with the sucrose surface. Starting from s addition of hexose + salt in the right constant proportion will transfer the composition of the liquid phase via the point representing the minimum sucrose-water ratio and r to q . It can easily be shown that the purity of the liquid phase at c is less than at a and that r represents a minimum purity, obtainable through evaporation of water. Between r and q the purity will rise when water is removed by evaporation.

A point of minimum purity occurs only if it is possible to draw from O a tangent to srq . Since we do not know the shape of srq , there is no proof that such a point of minimum purity actually exists. The existence of such a point would however explain some observations made by CLAASSEN on beet and cane molasses¹⁸. It is obvious that there must be a point of minimum purity on each of the planes through OS and one of them will represent the lowest purity possible. This would be the 'ideal' molasses at 30° C.

It is not within the scope of phase rule considerations to provide an explanation for the depression occurring in the sucrose surface. Existence of soluble compounds between two or more of the components might provide an explanation, but the occurrence of the depression in the sucrose surface does not necessarily prove the existence of such compounds, and as long as they do not separate under certain conditions, nor show their existence by discontinuities of the solubility curves, other means of proving their existence will have to be found (see p. 524).

Hence PRINSEN GEERLIGS' hydrated sugar-salt compounds would fit in the quaternary model developed by VAN DER LINDEN by explaining the depression in the sucrose surface, but the hypothesis of their existence is not indispensable. If however final molasses has to be seen as an eutectic mixture, PRINSEN GEERLIGS' hypothesis is redundant.

It is easy to see how multicomponent compounds will affect the quaternary model if they separate. Their existence will be shown by a new face, for example that show as abc in Fig. 14/3. In this case the melting point of the compound will have to be above 30° C. If, on the other hand, the final

crystallisation temperature is the higher one, the compound cannot exist as a solid at 30°C and surface *abc* will not occur. Such a compound would be represented by a point inside the undersaturated polyhedron.

VAN DER LINDEN has not gone further than explaining equilibrium conditions in final molasses on the basis of a four component model in which he discerned between salts and hexose. BIRKETT¹¹ has drawn practical conclusions from a three component diagram grouping all nonsucrose substances as one component. KELLY¹² however has criticised such simplifications by pointing to the rather significant difference in behaviour in respect of solubilities between dextrose and levulose. By plotting the composition of six samples of molasses in a diagram showing the equilibrium conditions of sucrose, levulose and dextrose, he is led to conclude that the dextrose/levulose ratio exercises some directive influence on the limitation of sucrose crystallisation. In this example the effect of the salts present was however not taken into account and generally speaking KELLY's observations can be seen as a desirable extension of VAN DER LINDEN's fundamental expositions.

(a) Eutectic Mixture versus Saturated (Metastable) Solution of Sucrose

In the foregoing pages it has been explained that molasses has to be regarded either as an eutectic mixture (JESSER) or as a solution of sucrose saturated at 30°C , if 30°C is the temperature to which low grade massecuite is cooled in the factory and equilibrium is attained. VAN DER LINDEN has shown how to decide which of the two alternatives is the correct one.

If molasses is an eutectic undercooled mixture, its purity will not rise if heated together with sucrose crystals until the temperature is reached where the sample is just saturated in respect of the second component. If molasses is a saturated (stable or metastable) solution its purity will rise immediately if heated together with sucrose crystals.

Preliminary tests carried out by VAN DER LINDEN¹³ were not conclusive, but HELDERMAN¹⁴ showed that the purity of a sample of saturated molasses rose immediately when heated with sucrose crystals. Before carrying out his tests HELDERMAN had carefully ascertained that his molasses was free from microscopic grain. This precaution had become necessary after KALSHOVEN¹⁵ had shown that undiluted factory molasses which has been kept for some time is hardly ever free from microscopic grain.

HELDERMAN's investigation has certainly proved that final molasses is not an eutectic mixture in the sense meant by JESSER, *i.e.* where the inability of crystallisation of *n* prevents further crystallisation of sucrose.

KELLY¹² however has correctly pointed out that molasses is generally saturated with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and that it is well known that sucrose and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will crystallise simultaneously. In Hawaiian molasses, sucrose and KCl have been observed to crystallise together¹⁶. Here we see that alternative (a) (see p. 523) prevails, for although the purity of the final molasses was unusually high crystallisation of sucrose was not altogether prevented.

On the other hand, some nitrogen compounds, *viz.* *L*-aspartic acid and *L*-tyrosine, in respect of which many molasses are saturated, seem, according to KELLY, to control the limit of crystallisation of sucrose.

More work is undoubtedly required to decide whether we have here an example of a true eutectic mixture.

(b) *The Estimation of Fine Grain in Final Molasses according to Kalshoven*

This method is based on the fact that the refractometer reading on a sample of final molasses which contains microscopic grain gives the refractometer brix of the liquid phase of the mixture. The difference between this brix value and the refractometer brix of the sample after dissolution of the microscopic grain depends on the quantity of grain originally present and this association permits the calculation of the latter quantity.

Dissolution of microscopic grain can be brought about either by heating, or by dilution with water. The actual quantity of water required (10 or 20% on molasses) should be estimated from a microscopic examination of the sample and should not be excessive. The diluted sample is analysed and from the results the composition of the original sample (grain being dissolved) is calculated. The latter composition should be given as:

$$\begin{aligned} a &= \% \text{ dry substance} \\ s &= \% \text{ sucrose} \\ p &= \text{refractometer brix} \\ x &= \% \text{ grain.} \end{aligned}$$

Further we term:

$$\begin{aligned} b &= \% \text{ dry substance of the liquid phase of the original sample} \\ q &= \text{refractometer brix of the liquid phase of the original sample} \\ y &= \% \text{ sucrose of the liquid phase of the original sample.} \end{aligned}$$

y and b cannot be determined directly.

The difference between a and p , and also between b and q , is due to the nonsucrose present in molasses.

Assuming straight proportionality

$$\frac{p - a}{q - b} = \frac{a - s}{b - y}.$$

Further, since

$$\frac{a - s}{b - y} = \frac{100 - x}{100},$$

we find

$$\frac{p - a}{q - b} = \frac{100 - x}{100},$$

and since

$$(100 - x) \times \frac{b}{100} + x = a$$

it follows that

$$x = \frac{100(a - b)}{100 - b}.$$

In this equation b cannot be determined directly and has to be estimated from our formulae.

$$100p - 100a = 100q - 100b - xq + xb$$

$$\frac{100a - 100b = 100x - xb}{100p = 100q + 100x - xq}$$

$$x = \frac{100(p - q)}{100 - q}$$

and finally

$$y = \frac{s(100 - q) - 100(p - q)}{100 - p}$$

from which the purity of the grain-free molasses can be calculated.

If the accurate determination of the refractometer brix is difficult due to the dark colour of the sample, it may be expedient to use reflected instead of transmitted light. The accuracy of the reading can further be enhanced by rotating the molasses in a half-filled bottle prior to the determination. Small air bubbles will be intimately mixed with the molasses forming a kind of froth which is brought in between the prisms¹⁷.

KALSHOVEN, testing a large number of Java final molasses, found many to contain microscopic grain in excess of 10%, which corresponds to a difference in purity between liquid phase and total molasses of more than 9 points.

3. Hydrated Sugar-Salt Compounds

Although probably no longer essential for a better understanding of the nature of final molasses, the existence of hydrated sugar-salt combinations is still rousing great interest amongst sugar chemists.

PRINSEN GEERLIGS' hypothesis¹⁸ was based on the work of older chemists (MAUMENÉ, PÉLIGOT, STENHOUSE and others) who had succeeded by slowly evaporating solutions of sucrose, glucose or fructose together with salts like NaCl, NaI, CaCl₂, CaBr₂, etc., in obtaining crystals supposed to be chemical compounds of, for example, the following composition: C₁₂H₂₂O₁₁·NaCl·12H₂O; (C₁₂H₂₂O₁₁)₂·3NaI·3H₂O, etc. But since it was not proved that these compounds were not mix-crystals (solid solutions), HELDERMAN undertook in 1920 to investigate the matter further. He determined the solubility at 30° C of sucrose as affected by the presence in increasing quantities of a number of salts, and also of these salts in the presence of increasing quantities of sucrose¹⁹, in an attempt to find out if the solubility curves would meet in an Invariant Point, or would be intersected by a third curve due to the crystallisation of a sucrose-salt compound. A similar investigation was carried out for glucose. Salts investigated were K₂SO₄, KCl, NaCl, K-acetate and K-oxalate. No proof of the formation of molecular compounds between sucrose, or glucose and one of the investigated salts was found, the solubility curves always met in an Invariant Point.

The investigation was criticised by KOLTHOFF²⁰ who pointed out that retardation of crystallisation might have been the cause of the non-separation of molecular sugar-salt compounds in HELDERMAN's experiments. He was able to show that at 18° C, and also at 30° C²¹ (after HELDERMAN had pointed out that his conclusions referred to 30° C)²² the compound C₁₂H₂₂O₁₁·NaCl·2H₂O is stable in contact with its saturated solution. This result has recently been confirmed by WIKLUND²³. Therefore the conclusion seems justified that of all hydrated compounds investigated, the existence of the NaCl combination only has definitely been proven. Similarly MATSUURA²⁴ has given convincing evidence for the existence of a glucose-salt combination, *viz.* C₆H₁₂O₆·NaCl·H₂O. But the problem still to be solved is: do such hydrated compounds actually exist in molasses and do they affect the crystallisation of sucrose, or do they merely affect the shape of the sucrose face (see p. 519).

Recently the matter has been approached in a novel way by WIKLUND and by SCHNEIDER. According to WIKLUND²⁵ the most expedient method to decide upon the existence of molecular compounds between sugars and salts in a sucrose and salt containing solution is to study how a prominent

property of such a solution varies when the concentration of the components is altered. Obviously such a study is more likely to give positive results when salts are used, of which a molecular compound with sucrose has already been made likely to exist by other means. The property selected by WIKLUND for his investigation was the optical rotation of the solution which is known to be affected by the presence of salts, possibly due to the formation of compounds. WIKLUND prepared equimolecular solutions of sucrose and salts which were mixed in differing proportions. The optical rotation of each mixture was measured and the result compared with the rotation as calculated on the assumption that the specific rotation of sucrose is not affected by the presence of salts, *i.e.* that no molecular compounds having their own specific rotation are formed. WIKLUND was able to show (for different total concentrations) that the maximum difference between observed and calculated rotation occurred when sucrose and salt were mixed in equimolecular proportion and accepts this fact as a positive indication of the existence of molecular compounds in solution.

Salts studied were KCl, NaCl, KBr, NaBr, KI, NaI and Na-acetate. A secondary conclusion was that the formation of the NaCl compound is limited, but of the Na-acetate compound prominent. This seems to be in accordance with the observation by HELDERMAN, and also LEBEDEFF, that sodium acetate containing solutions of sucrose are extremely viscous.

WIKLUND's results are in accordance with earlier results obtained by VAN HOOK²⁶. VAN HOOK examined synthetic molasses by means of their X-ray scattering patterns. From the X-ray diffraction patterns of desiccated sucrose-potassium nitrate solutions VAN HOOK concluded that the results favour the opinion that the sucrose in molasses is largely in the form of (amorphous) complexes.

On the other hand, SCHNEIDER²⁷, who studied the infrared spectra of desiccated beet molasses, could not find any evidence of sugar-salt compounds in final molasses.

4. Solubility of Sucrose in Solutions also Containing Nonsucrose Components

VAN DER LINDEN's examination of equilibria in multi-component systems containing sucrose is of a semi-quantitative nature and has served a useful purpose by providing a general background against which quantitative data illustrating the actual equilibria can be considered.

The results of many extensive investigations on the solubility of sucrose in systems which also contain salts, glucose and fructose have been published

Since the molasses problem attracted the attention of chemists all over the world. Amongst the older studies the work of SCHUKOW and KÖHLER, later that of VAN DER LINDEN and HELDERMAN, and more recently that of JACKSON and SILSBEE, and in particular that of KELLY, who not only studied a ternary, but also a quaternary and a quinary system, should be mentioned. These investigations are fully discussed elsewhere in this book.

Of particular interest is the effect of invert sugar on the solubility of sucrose. This system was studied by JACKSON and SILSBEE²⁸. SIJLMANS²⁹ gave JACKSON and SILSBEE's results in a particularly convenient table which is shown here as Table 1.

5. The Rate of Crystallisation of Sucrose from Impure Solutions

The amount of sucrose lost in final molasses depends on the amount of water present in this material, and the prevailing ratio of sucrose to water. This ratio is equal to the solubility only if equilibrium is attained. At the end of the crystallising process this is hardly ever the case, due to crystallisation of sucrose having become extremely slow as the purity and the temperature of the massecuite dropped. Hence for a proper understanding of the molasses problem a thorough knowledge of the factors which influence the rate of crystallisation of sucrose is indispensable. The old hypothesis, first formulated by FELTZ³⁰ that viscosity of molasses is the main factor responsible for the retardation of the crystallisation is no longer accepted as correct, but sometimes still referred to. The factors which do affect the rate of crystallisation are discussed in Chapter 4 of this book. Their importance is also illustrated by Hawaiian experience which showed in 1946 that it took a longer time than before for crystallisation to proceed to the point where the saturation temperature is reduced to the standard of 50° C. The changed nature of the 1946 low grade material was responsible for at least 50% more time being required to obtain the same amount of crystallisation as in former years³¹.

6. Some Practical Considerations

The nature of PRINSEN GEERLIGS' hypothesis of hydrated sugar-salt compounds has probably not stimulated many attempts to reduce the purity of final molasses. Sucrose was supposed no longer to be present as a free component and hence could not crystallise whatever one did.

To a certain extent the same can be said of the conception of molasses being an eutectic mixture. Here the presence of certain nonsucrose consti-

TABLE 1

SOLUBILITY OF SUCROSE IN WATER (g PER 100 g) ALSO CONTAINING INVERT SUGAR AND AT DIFFERENT TEMPERATURES (JACKSON AND SILSBEE)

Temp. °C	g invert sugar/100 g water												
	0	100	110	120	130	140	160	180	200	220	240	260	280
30	214	182	180	177	175	172	168	164	160	157	154	151	149
31	216	184	182	179	177	174	170	166	162	159	156	153	151
32	218	187	184	182	179	177	173	169	165	161	158	156	153
33	221	189	186	184	181	179	175	171	167	163	160	158	156
34	223	191	189	186	184	181	177	173	169	166	163	160	158
35	225	193	191	188	186	183	179	175	172	168	165	163	161
36	228	196	193	191	188	186	182	178	174	170	167	165	163
37	230	198	195	193	190	188	184	180	176	173	170	167	165
38	232	200	198	195	193	190	186	182	178	175	172	170	168
39	235	202	200	197	195	192	188	184	181	177	174	172	170
40	237	205	202	200	197	195	191	187	183	180	177	175	172
41	239	207	204	202	199	197	193	189	185	182	179	177	175
42	242	209	207	204	202	199	195	191	188	184	181	179	177
43	244	211	209	206	204	201	197	193	190	186	184	182	179
44	246	214	211	209	206	204	200	196	192	189	186	184	182
45	249	216	213	211	208	206	202	198	195	191	188	186	184
46	251	218	216	213	211	208	204	200	197	193	191	189	187
47	253	220	218	215	213	210	206	202	199	196	193	191	189
48	256	223	220	218	215	213	209	205	201	198	195	193	191
49	258	225	222	220	217	215	211	207	204	200	198	196	194
50	260	227	225	222	220	217	213	209	206	203	200	198	196
51	263	229	227	224	222	219	215	211	208	205	202	200	198
52	265	232	229	227	224	222	218	214	211	207	205	203	201
53	267	234	231	229	226	224	220	216	213	209	207	205	203
54	270	236	234	231	229	226	222	218	215	212	209	207	206
55	272	238	236	233	231	228	224	220	218	214	212	210	208
56	274	241	238	236	233	231	227	223	220	216	214	212	210
57	277	243	240	238	235	233	229	225	222	219	216	214	213
58	279	245	243	240	238	235	231	227	224	221	219	217	215
59	281	247	245	242	240	237	233	229	227	223	221	219	217
60	284	250	247	245	242	240	236	232	229	226	223	222	220
61	286	252	249	247	244	242	238	234	231	228	226	224	222
62	288	254	252	249	247	244	240	236	234	230	228	226	225
63	291	256	254	251	249	246	242	238	236	232	230	229	227
64	293	259	256	254	251	249	245	241	238	235	233	231	229
65	295	261	258	256	253	251	247	243	241	237	235	233	232
66	298	263	261	258	256	253	249	245	243	239	237	236	234
67	300	265	263	260	258	255	251	247	245	242	240	238	236
68	302	268	265	263	260	258	254	250	247	244	242	240	239
69	305	270	267	265	262	260	256	252	250	246	244	243	241
70	307	272	270	267	265	262	258	254	252	249	247	245	244
71	309	274	272	269	267	264	260	256	254	251	249	247	246
72	312	277	274	272	269	267	263	259	257	253	251	250	248
73	314	279	276	274	271	269	265	261	259	255	254	252	251
74	316	281	279	276	274	271	267	263	261	258	256	254	253
75	319	283	281	278	276	273	269	265	264	260	258	257	255

tients in respect of which molasses is also saturated, prevents further crystallisation of sucrose. And unless such constituents are specifically removed by an improved clarification process (as suggested by KELLY¹² in respect of certain amino acids) further exhaustion of final molasses cannot be anticipated.

Only if molasses is seen as a saturated solution of sucrose, can further exhaustion be expected either by reducing the water content or lowering the temperature, or both.

Fortunately practical attempts to reduce the purity of final molasses have not waited until the final answer to the theoretical considerations was given.

In 1919 VAN DER LINDEN¹³ published results of exhaustibility tests in which samples of molasses of increasing concentration were rotated in bottles at 30° and 50° C with sucrose crystals for such a period that equilibrium was probably established. The samples chosen for this investigation were undiluted factory molasses from which fine grain was removed by dilution and heating. Afterwards they were concentrated to the required density. Without any exception it was possible to bring all molasses to a purity lower than that achieved in the factory. The difference between factory purity and minimum purity achieved in the test was however quite different for different molasses, and molasses with a higher purity were sometimes found to have been better exhausted in the factory than molasses with a lower purity.

In some cases a minimum was found in the curve showing sucrose % water as a function of nonsucrose % water, a possibility which was foreseen when the theoretical curve shown in Fig. 14/5 was discussed.

The slope of the curve showing the relationship between purity and concentration differed considerably for different samples, but in many cases tended to become horizontal near a dry matter percentage of 85, at least at 30° C. The difference between the purities obtained at the same concentrations at 30° and 50° C tended to become smaller for higher concentrations, in agreement with theoretical considerations.

The combination of the realisation that exhausted molasses is a saturated solution of sucrose and the results of exhaustibility tests as conducted by VAN DER LINDEN and others has not failed to reduce purities as achieved in factories.

The question to answer was: what are the conditions for a maximum crystallisation of sucrose? Boiling to a higher brix was soon found to be useful, and also cooling to a lower temperature. To overcome the objection that this would make the massecuite too stiff to manipulate (for addition of water in the crystallisers was not permitted) VAN DER LINDEN³² recom-

mended adding about 15% of slightly diluted final molasses to the masse-cuite when leaving the crystallisers in order to 'lubricate' the heavy mixture.

7. Exhaustibility of Final Molasses

If final molasses were an eutectic mixture, as suggested by JESSER, there would be an 'absolute minimum purity', and at that purity the molasses would be 'theoretically exhausted'. The same might be the case if at a certain stage the withdrawal of more water from a sample of molasses resulted in an increased solubility of sucrose (see p. 519).

Since, however, it seems to be normal for the solubility to decrease as more water is withdrawn, the purity of the sample also will decrease. Admittedly water cannot be withdrawn *ad libitum* and moreover it becomes more and more difficult to reach saturation as the water content drops. For these reasons we have to accept a practical lowest purity which is extremely difficult to exceed, but this purity should not be called the 'absolute minimum purity', nor should molasses of this purity be termed 'theoretically exhausted'.

Tests in which the withdrawal of water by evaporation at a low temperature is continued to the stage where subsequent attaining of saturation in respect of sucrose is expected still to be practicable under favourable conditions, are called exhaustibility tests or boiling down tests. Attaining equilibrium usually takes a considerable period of time (weeks, months) and for this reason the purity attained in an exhaustibility test is generally lower than that obtainable in a factory where unlimited crystalliser capacity is not available. The purity of an exhaustibility test can, however, be seen as the ideal purity to be aspired to and is often called the target purity of the particular material. The term expected purity is also used, but perhaps less correctly.

Target purities are dependent on the particulars of the exhaustibility test. For this reason standardisation of exhaustibility tests is desirable when their results have to be compared. International agreement on the manner in which the results are expressed is also desirable. A considerable amount of confusion exists in the data provided by different authors, making comparison of results an often impossible task. It is necessary to state, whether sucrose has been determined by single polarisation, or by which modification of CLERGET's method, whether the water percentage has been found by drying, or by using a refractometer, or has been derived from a gravity brix as determined in a diluted solution of the molasses, and whether glucose means the total amount of reducing sugars, or dextrose only, and so forth.

Generally speaking it is advisable to use true purities so as not to introduce additional variables due to the difference between true solids and refractometer and spindle brix, or between direct pol and the sucrose percentage as determined by the JACKSON and GILLIS method.

HONIG³³, however, for the sake of simplicity, recommends substituting apparent for true purities, but whether such a substitution does reduce the value of a target purity as a basis of comparison for working purities, is still an open question. In Hawaii refractometer brix is generally used, and specific conductivity instead of ash (see p. 549).

Owing to the fact that purity alone is not a suitable measure of the state of exhaustion of a molasses, but must be interpreted in relation to the lowest purity attainable in practice with that molasses, MICHELI and DE GYULAY³⁴ developed quantitative definitions for 'exhaustibility' and 'state of exhaustion'. The term 'exhaustibility' was proposed for use as a measure of the readiness of a molasses to exhaust to a low purity and was defined by the equation:

$$E_0 = 100 - Q_L$$

where

$$E_0 = \text{exhaustibility}$$

and

$$Q_L = \text{the lowest true purity obtainable in a standardised exhaustibility test with the particular material.}$$

The term 'state of exhaustion' was to be used as a measure of the relationship of the actual true purity of a molasses to Q_L and was defined by the equation:

$$E = \frac{100 - Q}{100 - Q_L}$$

where

$$E = \text{state of exhaustion}$$

and

$$Q = \text{actual true purity of the molasses.}$$

Unfortunately these expressions have not been generally accepted.

The target purity attained in an exhaustibility test is controlled by those factors which govern the amount of water to be left behind in the sample and the solubility of sucrose under the prevailing conditions. Both factors are closely connected to the composition of the nonsucrose of the particular

material. Hence there must be some relationship between the target purity of a final molasses and the composition of the nonsucrose, and if it is possible to characterise the composition of the nonsucrose by a few simple data it should be possible to associate target purities with nonsucrose composition in a simple formula.

It is even not unreasonable to expect a similar relationship between nonsucrose composition and the purities attained under normal working conditions, but since factory molasses are usually supersaturated, and since their water content depends among other things on the available factory plant, the expected relationship may be somewhat obscure.

(a) *Statistical Target Purities*

The relationship between purity and nonsucrose composition has been extensively studied by SIJLMANS³⁵. SIJLMANS submitted to a statistical analysis the composition of a large number (78) of Java factory molasses from which fine grain had been removed and which had been given ample time to reach equilibrium at room temperature (30° C) in respect of solid sucrose.

The composition of the samples was given in terms of sucrose (double polarisation), refractometer brix, hexose (no differentiation between glucose and fructose), sulphated ash (not corrected by deducting 10%) and gums. Hence nonsucrose was refractometer brix – sucrose, water was 100 – refractometer brix, and purity was sucrose: (100 – refractometer brix) × 100.

In the first place SIJLMANS established for his set of samples the existence of a close relationship between purity and concentration. The more concentrated the molasses, the lower the purity.

SIJLMANS – to illustrate this relationship – plotted in a diagram sucrose % nonsucrose against water % nonsucrose and found a fairly straight line, dropping from 64 to 40% sucrose on nonsucrose for a drop of 35 to 22% water on nonsucrose.

Next he tried to establish whether the amount of sucrose held in solution by the moisture present in the samples was in any way connected to the quantity of any of the nonsucrose constituents present.

In the first place the effect of hexose on the solubility was examined and a negative correlation was found. More hexose % water was associated with less sucrose % water in agreement with VAN DER LINDEN's result that invert sugar reduced the solubility of sucrose, and *vice versa*. Generally the solubility of sucrose in his samples appeared to coincide within fairly

narrow limits with the relevant part of VAN DER LINDEN's solubility curve which is represented by the formula:

$$\text{sucrose \% water} = (a_t - 13) - 0.22 (\text{hexose \% water})$$

where a_t is the solubility of sucrose in water at t° according to HERZFELD.

A similar investigation into any effect of other nonsucrose constituents on the solubility of sucrose yielded negative results, *i.e.* the curves for sucrose % water plotted against ash % water, and against gums % water appeared to be nearly horizontal. From this outcome SIJLMANS concluded that the solubility of sucrose in the water present in final molasses is influenced by hexose only, not by other nonsucrose ingredients.

Hence the formula given above could be used to estimate the amount of sucrose any final molasses should contain according to this hypothesis and the corresponding calculated purity could be compared with the actual purity. It would, however, be incorrect to call the calculated purity a target purity. It is merely a target purity calculated on the basis that hexose is the only nonsucrose constituent which controls sucrose solubility.

So far we have defined target purities as purities resulting from exhaustibility tests, but we have pointed to the probability that target purities can mathematically be associated with data indicating the composition of the nonsucrose.

SIJLMANS' second paper³⁵ deals with a study of deriving target purities – called by him 'practical exhaustibility' – from data illustrating nonsucrose composition. For this purpose the composition of 90 Java molasses was statistically examined.

Unfortunately the true moisture content of the samples was not known. They were calculated by using certain formulae derived earlier by SIJLMANS³⁶. These formulae show the general relationship between degrees brix (determined pyknometrically in a 1 to 10 dilution), the sulphated ash content, and the moisture content of molasses produced by the three methods of juice clarification. They are:

Defecation final molasses:

$$\% \text{ moisture} = 100 - (\text{pyknometer brix} - 0.72 \times \text{sulphated ash percentage}).$$

Sulphitation final molasses:

$$\% \text{ moisture} = 100 - (\text{pyknometer brix} - 0.86 \times \text{sulphated ash percentage}).$$

Carbonatation final molasses:

$$\% \text{ moisture} = 100 - (\text{pyknometer brix} - 0.74 \times \text{sulphated ash percentage}).$$

In the first place SIJLMANS calculated for each molasses the solubility quotient, *viz.* the ratio between the amount of sucrose actually present per

100 parts of water and the amount of sucrose which should be present according to his solubility hypothesis*.

The solubility quotients calculated varied between 0.816 and 1.440. SIJLMANS then rejected those molasses whose solubility quotients were either > 1.05 or < 0.95 , and continued to investigate statistically the composition of the remaining group of 37 molasses.

He found that a high ash content of the nonsucrose generally correlated with a low nonsucrose concentration (= nonsucrose % water) and hence with a high purity. Further that a high ash content of the nonsucrose generally also correlated with a high ash concentration (= ash % water). Further that for those molasses showing a high ash concentration the temperature of spinning had usually been higher than for the molasses showing a low ash concentration, and finally that a high nonsucrose concentration generally coincided with a high spinning temperature.

He concluded that the ash content of the nonsucrose affects the purity actually obtained to a significant extent, because the ash concentration, according to the spinning temperature limits the nonsucrose concentration obtainable under normal working conditions.

SIJLMANS further assumed that the relationship between ash concentration and temperature, as affecting nonsucrose concentration, should be expressed as ash % moisture - t , and plotted in a diagram ash % moisture - t against ash % nonsucrose. First, however, the data for ash % moisture were corrected so as to bring the solubility quotient exactly to unity.

The diagram showed a strong relationship between the values for ash % moisture - t and ash % nonsucrose and it was possible to draw a straight line linking those molasses for which ash % moisture - t , relative to ash % nonsucrose had a maximum value.

SIJLMANS then selected 11 molasses whose points were situated nearest to this straight line and assumed that they were truly satisfactorily exhausted molasses. For these samples he examined the possibility of associating their purities with the composition of their nonsucrose, and to typify nonsucrose he selected the values ash % (nonsucrose - ash - hexose) and hexose % (nonsucrose - ash - hexose). He derived the following formula:

$$x_1 = 50.073 + 0.30615 x_2 - 0.09789 x_3$$

where

$$x_1 = \text{sucrose \% nonsucrose}$$

$$x_2 = \text{ash \% (nonsucrose - ash - hexose)}$$

$$x_3 = \text{hexose \% (nonsucrose - ash - hexose)}.$$

* SIJLMANS now used JACKSON and SILSBEE's solubility data.

The purity calculated with the formula $\frac{100 x_1}{100 + x_1}$ was termed by SIJLMANS the practical exhaustibility of final molasses, which is a target purity in the sense described earlier.

The basis of this target purity is the assumption that final molasses should be concentrated until the so-called optimum ash concentration is attained and that the amount of sucrose which should be present in the amount of water then left behind in the molasses corresponds to JACKSON and SILSBEE's sucrose solubility table. Hence the optimum ash concentration is an important factor in SIJLMANS' method of judging molasses purities. The optimum ash concentration can be calculated with the following formula:

$$\gamma_2 = 1.6665 \gamma_1 + 0.9946 \gamma_3 - 3.392$$

in which

$$\gamma_2 = \text{ash \% water}$$

$$\gamma_1 = \text{ash \% nonsucrose}$$

$$\gamma_3 = \text{spinning temperature in } ^\circ\text{C.}$$

SIJLMANS' criteria have been used in the Java sugar industry for a considerable period with a fair degree of success.

One should appreciate however that SIJLMANS' hypothesis that the solubility of sucrose in final molasses is affected by hexose only and not by other nonsucrose constituents has not experimentally been confirmed by him. THIEME³⁷ drew attention to the fact that some information on this point could be derived from data published by CLAASSEN, VAN DER LINDEN and HELDERMAN, and completed the available data by carefully conducting some more solubility tests.

The solubility determinations of CLAASSEN and VAN DER LINDEN indicated roughly that the higher the purity of the substance investigated, the higher the solubility quotient. This relationship was confirmed by HELDERMAN's data which were more accurate due to the care given to the removal of microscopic grain*. THIEME's solubility tests were carried out at room temperature on syrup and molasses of different purities. These liquors were saturated with sucrose and analysed. They yielded the solubility quotients shown in Table 2.

* KELLY⁶⁰ discerns between molasses with a good and with a bad solubility characteristic. A molasses with a good solubility characteristic is one in which the solubility quotient falls distinctly with fall in purity. One with a bad solubility characteristic is one which rises with fall in purity. Other authors do not seem to have found molasses with bad solubility characteristics, the drop in the solubility quotient with drop in purity generally being accepted as normal.

TABLE 2
SOLUBILITY QUOTIENTS ACCORDING TO THIEME AND SIJLMANS

Purity	Solubility quotient (THIEME)	Solubility quotient (SIJLMANS)	
		$b = 35$	$b = 60$
30	0.65	0.85	0.76
30-35	0.65-0.70	0.85-0.88	0.76-0.80
35-42	0.70-0.75	0.88-0.90	0.80-0.84
42-50	0.75-0.80	0.90-0.93	0.84-0.88
50-58	0.80-0.85	0.93-0.95	0.88-0.91
58-68	0.85-0.90	0.95-0.96	0.91-0.94
68-86	0.90-0.95	0.96-0.99	0.94-0.98
86-100	0.95-1.00	0.99-1.00	0.98-1.00

The next step was to compare these experimentally found solubility quotients with those calculated by SIJLMANS' method.

For this purpose SIJLMANS' formula was transformed into

$$\text{solubility quotient} = \frac{100}{100 + 0.22 b \left(\frac{100 - R}{R} \right)}$$

in which

b = hexose % nonsucrose

R = purity final molasses.

Table 2 also shows the solubility quotients calculated with this formula for hexose % nonsucrose values of 35 and 60, and for purities ranging from 30 to 100.

THIEME's quotients are lower than those calculated with SIJLMANS' formula and THIEME concluded that although the influence of the reducing sugars on the solubility of sucrose is most pronounced, the other nonsucrose constituents also have some effect. For this reason he preferred his empirical data to the quotients calculated according to SIJLMANS.

The applicability of SIJLMANS' method of judging the exhaustion of final molasses was investigated by BEHNE³⁸ for Queensland conditions.

By a method similar to that of SIJLMANS he derived the formula:

$$A = 45.93 + 0.01311 X - 0.2679 B$$

where

A = practical exhaustibility expressed as true purity

X = sulphated ash % other organic matter

B = reducing sugars % other organic matter.

The value of this formula for judging the actual purities of Queensland final molasses was originally thought promising, but a more detailed inves-

tigation by BEHNE³⁹ completely negated any hope of its use in that country.

Although SIJLMANS' formula has been applied in Java with a fair degree of success for a number of years, certain demerits became gradually more apparent. One of these shortcomings was that carbonation factories were more severely judged by the application of the formula than sulphitation and defecation factories.

In 1940 DOUWES DEKKER⁴⁰ published a paper in which SIJLMANS' approach to the problem was extensively discussed. He concluded that SIJLMANS' assumption that the 11 molasses selected to form the basis of his formula were truly satisfactorily exhausted was not sufficiently supported by factual evidence, and also that the hypothesis that the solubility of sucrose in molasses is merely influenced by hexose and not by the other nonsucrose constituents was not in accordance with the results of exhaustibility tests carried out earlier by VAN DE KREKE⁴¹.

He agreed, however, that SIJLMANS had correctly assumed that sulphated ash % nonsucrose and hexose % nonsucrose were by far the most important factors controlling the exhaustibility of final molasses. Hence it should be possible to calculate a formula showing the relationship between these variates and the purities of final molasses exhausted in standardised exhaustibility tests. DOUWES DEKKER, however, did not calculate such a formula, but the regression formula, showing the association of the purities of 150 final molasses produced in Java in 1938 and 1939 and the variates ash % nonsucrose and hexose % nonsucrose. The purity calculable with this formula for any final molasses whose nonsucrose composition is known is a target purity – not the target purity which would have been attained in an exhaustibility test, but the purity which would have been attained by the 'average Java factory' of the above mentioned years, just before World War II. The performance of the 'average 1938/39 Java factory' is the target set by DOUWES DEKKER's formula. It is obvious that factories equipped with modern crystallisation and centrifuging plant will find no difficulty in producing final molasses of a lower purity than indicated by this formula.

DOUWES DEKKER actually calculated four formulae, one from the molasses produced in defecation factories, and the others referring respectively to sulphitation and carbonation molasses, and to all molasses no matter what method of juice clarification was used. They are:

$$\begin{aligned} Y_w &= 35.886 - 0.08088 x_1 + 0.26047 x_2 \text{ (generally applicable)} \\ Y_d &= 32.947 - 0.05536 x_1 + 0.31269 x_2 \text{ (defecation factories)} \\ Y_{su} &= 38.208 - 0.10991 x_1 + 0.22104 x_2 \text{ (sulphitation factories)} \\ Y_{ca} &= 33.798 - 0.05108 x_1 + 0.30813 x_2 \text{ (carbonation factories)} \end{aligned}$$

where

α_1	= hexose % nonsucrose
α_2	= sulphated ash % nonsucrose
Y	= sucrose/dry matter purity
nonsucrose	= dry matter minus sucrose.

DOUWES DEKKER's formula, although developed for Java conditions, has also been applied with a certain measure of success in other countries, particularly Australia⁴². No evidence was found by VENTON to justify the need for individual factory corrections to the expected value determined with the formula and it was shown that the formula 'did not favour a particular district. Where certain mills lagged behind others it was apparent that this was due to the inadequate equipment and lack of control of the former'.

Many countries have developed their own formulae to calculate target purities. In Taiwan, WEI CHEN, TSUI-HOW HSU and PEI-CHI WANG⁴³ developed the following formula from the analysis of samples of final molasses from 36 factories over two consecutive milling seasons:

$$P = 19.787 + 0.2333 r + 0.4695 a$$

where

P	= theoretical true purity
r	= reducing sugars % nonsucrose
a	= ash % nonsucrose.

BAIKOW's conclusion⁴⁴ that a final molasses is properly exhausted if total sugars (sucrose plus reducing sugars) per 100 brix (determined in 1 : 1 dilution) are less than 59.1, although apparently of some value in Louisiana, did not apply to Indian conditions according to MATHUR⁴⁵. MATHUR prefers a maximum value for total sugars per 100 brix of 55.5, and also states that pol loss % cane should not be more than 1 %. The latter criterion obviously refers not only to the purity, but also to the quantity of final molasses produced.

Recently HONIG⁴⁶ criticised the DOUWES DEKKER formula and the Hawaiian method (see p. 549) of calculating target purities on the grounds that sucrose, dry matter and refractometer solids respectively are used as variates instead of pol and brix data on which factory control systems in the overwhelming majority of the cane sugar mills are based. He introduced the conception, apparent target purity, which according to the Java standard should be calculated by the formula

$$A.T.P. = 24.0 - 0.11 \text{ red. sugars \% nonsugars} + 0.26 \text{ ash \% nonsugars}$$

and according to the Hawaiian standard by the formula

$$A.T.P. = 20.0 - 0.13 \text{ red. sugars \%} \text{ nonsugars} + 0.28 \text{ ash \%} \text{ nonsugars}$$

(b) *Methods of Judging Purities of Final Molasses based on Exhaustibility Tests*

The basis of the formulae developed by SIJLMANS was also criticised by PAGNIER⁴⁷. He conducted a series of exhaustibility tests using final molasses of different Java factories at their natural water content and after equilibrium had been attained he found that the solubility quotients were with one exception lower than 1, in some cases considerably lower, *viz.* 0.82 and 0.86. He concluded that it is incorrect to assume that the sucrose solubility in final molasses is controlled by hexose only and that other factors also influence the solubility.

PAGNIER also pointed out that the correlations (see p. 532) on which SIJLMANS had based his conception of the maximum ash concentration were not very significant, and instead of accepting the ash concentration (relative to the temperature of spinning) as a criterion for the concentration at which final molasses should be spun off, rather preferred THIEME's criterion⁴⁸ which stated that the refractometer brix should be 85°.

THIEME's criterion did not differentiate between the optimum concentrations to which molasses of different composition should be concentrated, but PAGNIER thought this shortcoming of little practical importance. Generally PAGNIER drew attention to THIEME's method of judging purities of final molasses which had been used for a number of years by a group of Java factories. The results had been compared with the conclusions arrived at by applying SIJLMANS' formula and had generally been found to be of greater practical value.

According to THIEME's method the well mixed average sample of final molasses is first tested for microscopic grain. If present it is dissolved by adding a small amount (up to 10%) of water and heating. Next the sucrose percentage S_1 and the refractometer brix F_1 are determined, and the purity $R_1 = 100 \frac{S_1}{F_1}$ is calculated. The sample is now mixed with a sufficient quantity of sucrose crystals (ordinary white sugar is suitable) and placed in a weighing bottle in a large vacuum flask which is slowly rotated (one revolution in 7 minutes) at room temperature for about three weeks. The vacuum flask should be sufficiently large to accommodate 16–20 weighing bottles. After three weeks' rotation it is assumed that equilibrium has been attained, and without separating the crystals, the refractometer brix of the liquid phase F_2 is ascertained.

The purity of the saturated molasses is calculated with the formula:

$$R_2 = 100 \frac{S_1(100 - F_2) - 100(F_1 - F_2)}{F_2(100 - F_1)}$$

and R_3 is found using the graph shown in Fig. 14/6.

R_3 is the purity corresponding to a refractometer brix of 85° . The graph shown in Fig. 14/6 has been constructed by carrying out a large number of exhaustibility tests on different molasses of different water content, at room temperature. One finds the curve nearest to the point representing F_2 and R_2 and follows this curve until the horizontal line for 85° brix is intersected. The purity R_3 of this intersection is then read. R_3 is the purity the sample would have had if saturated at 85° refractometer brix. $R_1 - R_3$ indicates how far the original purity of the sample is removed from the target purity R_3 and is THIEME's final basis of comparison for judging the state of exhaustion of final molasses.

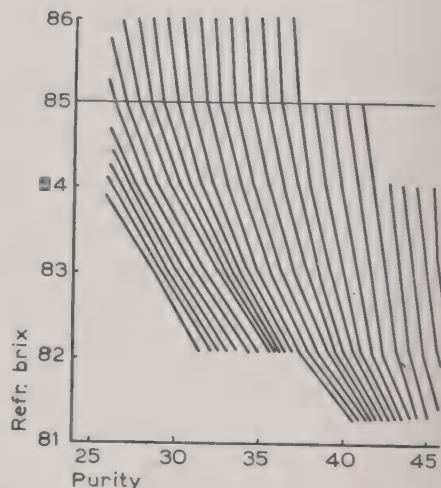


Fig. 14/6. PAGNIER's graph of converting purities to corresponding values at 85° refractometer brix.

DOUWES DEKKER⁴⁹ pointed out that although THIEME's method had successfully been applied the value of its results as criteria for judging the purity of final molasses largely depends on the applicability of Fig. 14/6 to molasses of a composition different from those which had served to construct the graph.

The difference $R_2 - R_3$, called Brix Influence by PAGNIER, reflects the drop in purity which could have been attained if the molasses had been spun off at 85° refractometer brix. A too low brix is usually related to particulars of the plant preventing a high concentration. As such PAGNIER mentions the diameter of the discharge valves of the pan, the strength of the stirring device of the crystallisers and the capacity and power of the centrifugals.

The difference $R_1 - R_2$ indicates the drop in purity which would have been obtained if the molasses had been spun off at the prevailing concentration and saturated at room temperature. This condition, of course, will never occur in actual practice and $R_1 - R_2$ is usually rather large, viz. 4.7–7.5 in examples given by PAGNIER. A value of zero would indicate that the molasses had been spun off undersaturated at the actual spinning tempera-

ture which is normally higher than room temperature. For this reason a positive value for $R_1 - R_2$ is to be expected and it requires some experience to judge what difference can still be considered normal and acceptable.

The subject of judging the state of exhaustion of final molasses by conducting exhaustibility tests and the factors affecting such state of exhaustion have also been studied by MICHELI and DE GYULAY³⁴. The authors reject the study of the exhaustion of molasses using phase rule methods since under factory conditions sufficient time is not available for the molasses and crystal in a low grade massecuite to reach equilibrium at the end of cooling in the crystallisers.

In their experiments the authors first adjust the moisture content of the (diluted) samples by evaporation in vacuo until the desired concentration is reached and then run them into an experimental crystalliser immersed in a water-bath which can be cooled from 75–45° C at about 1° C per hour. Sifted sugar is added and a stirring gear started. After crystallisation, molasses for analysis is separated through bolting silk in a pressure filter. The authors found by carrying out numerous tests that factors which sometimes are supposed to affect the rate of exhaustion, such as grain size, purity of massecuite, efficiency of stirring, etc. had very little direct effect on the final purity if varied over quite wide terms. The final temperature was found to have very little effect if reduced below 45° C, for the rate of exhaustion had already become very slow at 45° C.

With any given material there appeared to be only one factor, *viz.* concentration, which had any considerable effect on the final molasses purity. On the average a rise of 0.2 in the ratio of impurities to water gave unit decreases in the final purity. Accordingly, in order to find the lowest purity obtainable in practice with any given material, it is necessary to determine the maximum rate of impurities to water which can be attained with that material by the efficient use of modern plant under factory conditions.

As was set out above, THIEME and PAGNIER accept a target concentration of 85° refractometer brix for every molasses, independent of its composition. Earlier SIJLMANS had assumed that the ash concentration limits the practical maximum concentration at which a molasses can be spun. MICHELI and DE GYULAY state that the maximum ratio of impurities attainable in the factory depends on the nature of the molasses. They have found that with a 'free boiling' molasses the purity of the massecuite can be lower than with a 'poor' material.

If the 'poor' material were exhausted to the same concentration as attained

with the 'free boiling' molasses, a higher crystal to mother liquor ratio would result due to the higher purity of the massecuite. This higher ratio would mean a stiffer massecuite, which the available plant could not handle if it is assumed that the 'free boiling' material has been concentrated to its maximum value. Hence it is not practicable to concentrate the 'poor' material to such a high value and more water will be left in the molasses, corresponding of course to a higher purity. The factory working the 'poor' material has to be content with a lower concentration of its final molasses.

The authors did not have at their disposal quantitative data linking the nature of the molasses to the maximum concentration attainable in the factory under favourable conditions. Therefore they concentrated all the molasses of their experiments to the same nonsucrose : water ratio, *viz.* 3.5, although they thought that in actual practice a ratio of 4.5 might have been feasible.

For the molasses which were saturated at this concentration (3.5) they found that the ratios of reducing sugars to ash and of ash to total impurities both showed some correlation with the final purities, although there was a considerable scattering of the points. A higher reducing sugar to ash ratio meant a lower purity, a higher ash to impurities ratio corresponded to a higher purity.

The authors also calculated the solubility quotients* of their samples at the same purity (45.0) and the same temperature (45° C). For this purpose they applied a correction based on THIEME's data (see p. 534) reflecting the association between solubility quotient and purity, and the result of a former investigation, *viz.* that the solubility quotient of low grade molasses increases by approximately 0.0022 per 1° C rise in temperature. They constructed a curve, shown in Fig. 14/7, which gives the relationship between solubility quotient and final purity at 3.5 impurities/water ratio and suggest using this curve to judge whether the final purity obtained from a given material is as low as it should be. For this purpose the exhausted molasses filtered from a low grade massecuite is analysed for sucrose and water, and the saturation temperature is determined. The solubility quotient at 45° C and 45 true purity is calculated as discussed above, and the target purity associated with this solubility quotient is read from the curve of Fig. 14/7. The actual purity of the material is then compared with the target purity by computing the state of exhaustion.

* The authors use the expression 'saturation coefficient', but the term solubility quotient, introduced by SIJLMANS, seems more suitable.

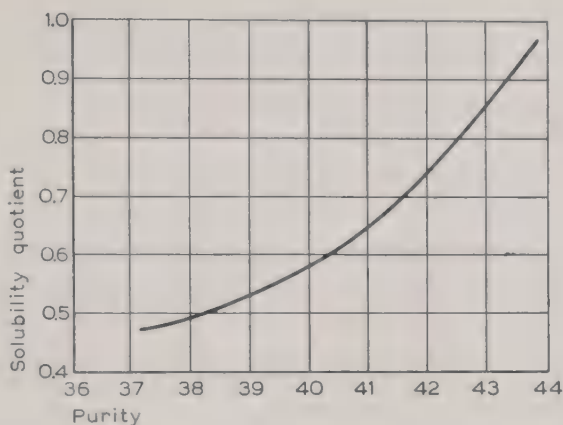


Fig. 14/7. Curve showing relationship between solubility quotient and purity at 45° C. (MICHELI and DE GYULAY)

When applying the above method of judging final purities it should be realised that the curve of Fig. 14/7 has been found by testing certain Queensland molasses and may not be applicable to any other material.

(c) *Viscosity and Exhaustibility*

The target purity of any final molasses is associated with the composition of the nonsucrose, firstly because the nonsucrose controls the solubility of sucrose (ratio sucrose/water at saturation), but also because the nature of nonsucrose very likely controls the minimum amount of water which has to be left behind in the molasses to enable further processing to run smoothly. Attempts – like that of SIJLMANS – to find a simple relationship between the composition of the nonsucrose and a target ratio of nonsucrose/water have not been successful.

Generalising, it can be said that removal of water from low grade massecuite in normal factory operations is continued to the stage where the massecuite can still be handled conveniently by the available plant, and it is not far-fetched to assume that the viscosity of the mother liquor is one of the main factors controlling the workability of the massecuite.

We also know that the performance of the centrifugals depends largely on the viscosity of the molasses spun off. These two considerations have led to the expectation that some advantage could be obtained by a target viscosity instead of a target nonsucrose/water ratio to be used as an intermediate step in computing target purities. Or in other words: final molasses as spun off in the centrifugals should be of a pre-agreed viscosity rather than of a standardised nonsucrose/water ratio. Generally speaking the target

purity should be such that powerful, modern equipment, particularly the centrifugals, can still satisfactorily handle massecuites containing molasses of this viscosity.

Realisation of the fact that viscosity is a major factor in the exhaustibility of final molasses necessitates a somewhat extensive discussion of this property.

Viscosity is the property which opposes the relative motion of adjacent portions of a liquid and can consequently be regarded as a type of internal friction. The coefficient of viscosity η is defined as the force per unit area, *viz.* dynes/cm² required to maintain unit difference of velocity, *i.e.* 1 cm/sec between two parallel layers 1 cm apart. The corresponding unit, *i.e.* 1 dyne/sec/cm², is called a poise, in honour of POISEUILLE. Since viscosity values in terms of this unit are usually small, subsidiary units known as millipoises (10⁻³ poise) or centipoises (10⁻² poise) are often used.

For many liquids the difference in velocity of the two layers 1 cm apart is always directly proportional to the force applied. Or: the rate of shearing is at all times a linear function of the shearing stress applied. Such liquids are said to be 'perfect' or 'Newtonian' in their flow properties, and their viscosity, *i.e.* the ratio of shearing stress to rate of shear, may thus be determined from the results of a single test in which the shearing stress and the rate of shear are determined.

Other liquids however do not respond similarly. Some offer an initial resistance to flow and will continue to do so until the stress is sufficient to overcome the initial resistance after which uniform shearing will take place. Fluids of this class exhibit the property of 'plasticity'. A third group of fluids, under stress, may exhibit pseudoplasticity. This type of flow resembles in part the flow of a Newtonian fluid and also that of a true plastic. No initial stress is required before shearing commences, but the rate of shear is not at once linear in its relation to the shearing stress. There appears to be a certain resistance to flow which does not prevent motion, but which for a time decreases with each successive increase in the rate of shear. When this resistance is completely overcome the linear relationship mentioned above is found to exist⁵⁰.

For the flow properties of a fluid to be studied it is necessary to select an instrument in which the rate of shear may be varied at will. With many types of viscosimeters (or viscometers) however this is not possible since the shearing stress applied throughout the test is constant.

ADKINS⁵⁰ has used a SEARLE type of viscometer designed by the staff of the Bureau of Experiment Stations at Brisbane to measure the viscosity of molasses and massecuites.

This viscometer consists essentially of a cylinder which is free to rotate in a test sample contained in a jacketted cylindrical vessel. The cylinder is driven by two equal masses supported in scale pans which are attached by cords passing over guide pulleys to a drum mounted on the shaft of the cylinder. The masses fall under the influence of gravity, and exert a constant torque on the drum; the cylinder thus rotates uniformly, at a rate which for a given mass depends only on the viscosity of the fluid in which the cylinder is immersed. The rate of shear of the fluid may readily be varied by altering the mass producing the shear.

ADKINS found that a number of samples of molasses tested exhibited pseudoplasticity to a slight degree, but the effect became less pronounced with increase in temperature. Hence for practical purposes a single correlation of mass and time of revolution sufficed to determine the viscosity of molasses, and practically any accepted device used for the measurement of the viscosity of opaque liquids may be adopted for molasses, according to ADKINS. He also found that massecuites exhibited pseudoplasticity to a much greater extent.

The lack of suitable instruments capable of measuring the viscosity of molasses has for a long time prevented a deeper investigation of this property, although viscosity measurements were introduced in the sugar industry as early as 1874.

The MACMICHAEL viscometer, studied by VAN DER LINDE, proved not altogether satisfactory⁵¹. In 1933, however, KNOP⁵² drew attention to the HOEPLER viscometer as an instrument suitable for measuring accurately the viscosity of final molasses. Although the HOEPLER viscometer is of the falling ball type where the shearing stress applied is constant, this instrument has found wide application in the sugar industry for the measurement of viscosity.

It was used by PRAEGER and HERON⁵³ when they investigated the effect of dilution and temperature on the viscosity of Queensland final molasses. They found the viscosity to be halved at 1.8% dilution on molasses. At higher concentrations the effect of temperature was very marked, 6° C increase being sufficient to halve the viscosity of undiluted molasses. They also found molasses to exhibit anomalous viscosity, *i.e.* not to give constant results when, for example, a sample was cooled and re-heated to the original temperature of determination. Similar results have been obtained by other authors, but a satisfactory explanation has never been given.

Another instrument, the STORMER viscometer, is also often used. The STORMER viscometer is similar to the SEARLE type viscometer and allows the shearing stress to be varied by altering the weights used to rotate the

cylinder. The STORMER viscometer was used by KING⁵⁴ in an investigation into the effect of brix (concentration), temperature and purity on the viscosity of final molasses.

The fact that all these variables affect viscosity makes it necessary to agree upon what is actually meant by 'the' viscosity of a final molasses.

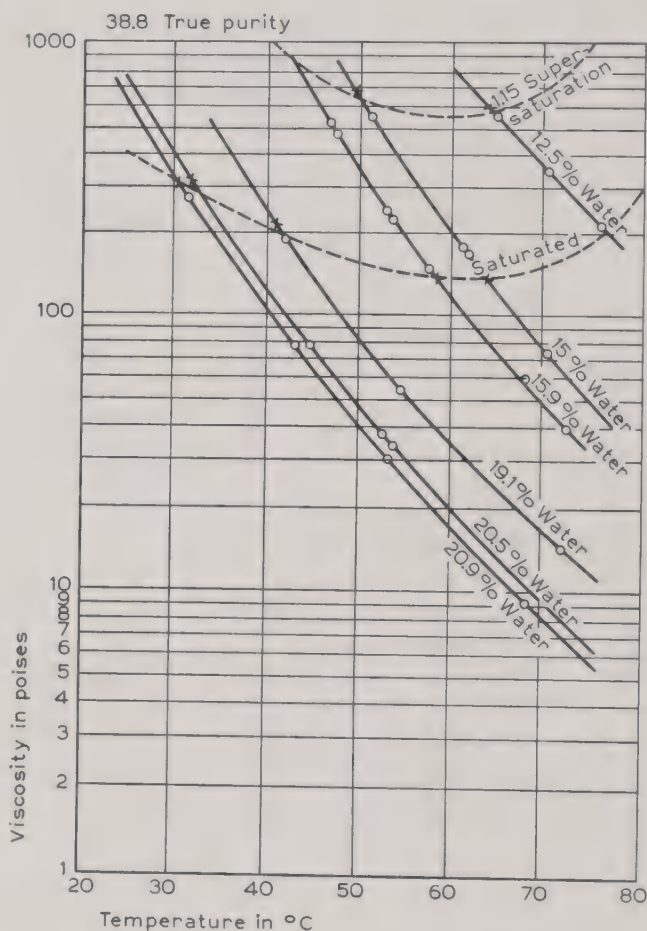


Fig. 14/8. Viscosities of members of one molasses family of equal purity. (MICHELI and DE GYULAY)

Molasses is a liquid mixture of sucrose, water and nonsucrose, the latter component also being a mixture of various ingredients. Molasses which differs only in respect of the ratios in which sucrose, water and nonsucrose are present, *i.e.*, molasses of identical nonsucrose composition is often said to belong to the same family. Hence the nonsucrose composition is typical for the family. Individual mixtures are either undersaturated, saturated or supersaturated, depending on the temperature at which they are considered.

Each member of one family exhibits its particular range of viscosities, according to temperature, and the question to answer is: is it possible to select from the infinite number of viscosities which can be exhibited by all members of one family, one which is typical of such a family?

This question has been studied in an investigation by MICHELI and DE GYULAY⁵⁵ who examined a number of Australian molasses at various conditions of temperature, purity and concentration. They give the results of this investigation in diagrams of which a typical one is shown in Fig. 14/8.

Fig. 14/8 illustrates the viscosity conditions of members of one family and of equal purity – in this case 38.8. Each continuous curve shows the change in viscosity with change of temperature of the members of the same moisture content. The curves given in Fig. 14/8 refer to 12.5 – 15.0 – 15.9 – 19.1 – 20.5 and 20.9 % water respectively. There is one temperature on each curve where the sample is just saturated. This temperature is marked by a cross. Consequently the broken line joining these crosses which cuts across the continuous curves shows the change in viscosity when the concentration of the solution is changed and the temperature simultaneously altered to keep the solution always saturated. Similar broken lines can be constructed for the solutions of certain degrees of supersaturation. In Fig. 14/8 the curve for 1.15 supersaturation is also shown.

MICHELI and DE GYULAY found that very often the curves indicating the change in viscosity with temperature of all saturated solutions of the same purity exhibit a distinct minimum. The saturation curve of Fig. 14/8 shows a minimum at approx. 60° C.

Fig. 14/9 shows similar curves for other molasses.

The region of the minimum viscosities is usually near 50–60° C. The practical conclusion to be drawn from this fact is that in order to ensure that final molasses is separated from the sucrose crystals at the point of minimum viscosity (for a certain purity) the method of heating to saturation in order to reduce viscosity of low grade massecuite which has been cooled in the crystallisers to say 35–40° C is in principle superior to the dilution method. In actual practice certain other factors have also to be taken into account, for example, the likelihood of dissolution of crystals due to local regions of undersaturation during either the heating or diluting procedure. The danger of dissolution is however larger when the massecuite is diluted after crystallisation.

As can be seen from Fig. 14/9 the minimum viscosity is not always very distinct, and in other cases there is a continuously decreasing viscosity with rise in temperature.

If there is a minimum viscosity, selecting this viscosity as typical of the

members of the same purity of one family seems an attractive suggestion. The whole family would then be characterised by the curve showing the change in the minimum viscosity with the alteration of the purity. The viscosity increases slowly at first, becoming more and more steep with

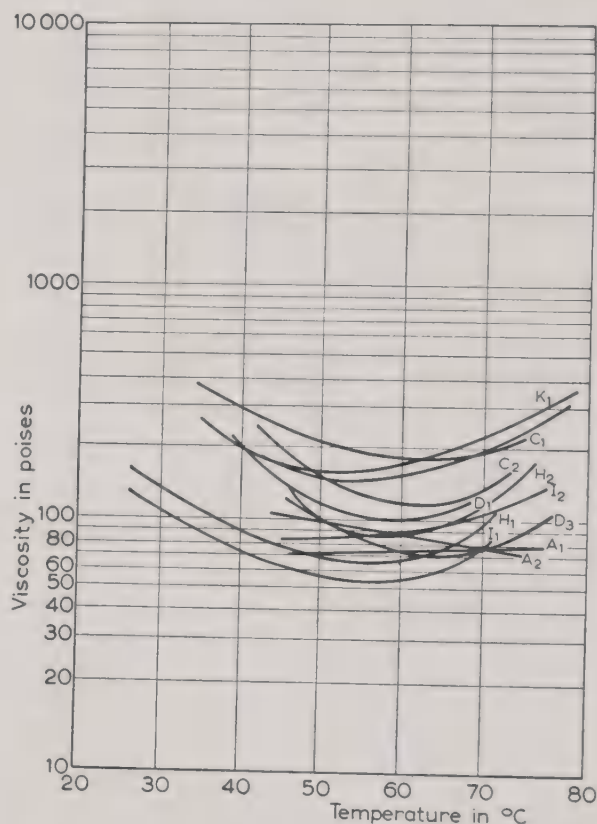


Fig. 14/9. Viscosities of saturated solutions of molasses at various temperatures. (MICHELI and DE GYULAY)

decrease in purity. As suggested by DOUWES DEKKER⁴⁹ it would probably be possible to select a point of the curve where a slight decrease of purity corresponds to a disproportionate increase in viscosity. If the viscosity of this point is not too high, for example less than 600 poises, the purity of this point of sudden increase in viscosity could be accepted as the target purity for the particular family, and the corresponding viscosity as the target viscosity. Insufficient data are however available to decide whether this method of finding the target purity of a family of molasses is practicable. Neither is any information available on the relationship between this type of target purity and the composition of the nonsucrose characteristic for the family.

The problem of using the viscosity as an intermediate step to arrive at a target purity has been solved in a practical way in Hawaii.

Instead of selecting the solution with the minimum viscosity as representative of all saturated solutions of the same purity, the solution saturated at 50° C was selected, and of all the solutions saturated at 50° C – which differ in concentration and purity – the solution exhibiting a viscosity of 600 poises was selected to represent the family. The purity of this solution was termed the target – or expected – purity for that family.

50° C and 600 poises were chosen for practical reasons, 50° C because

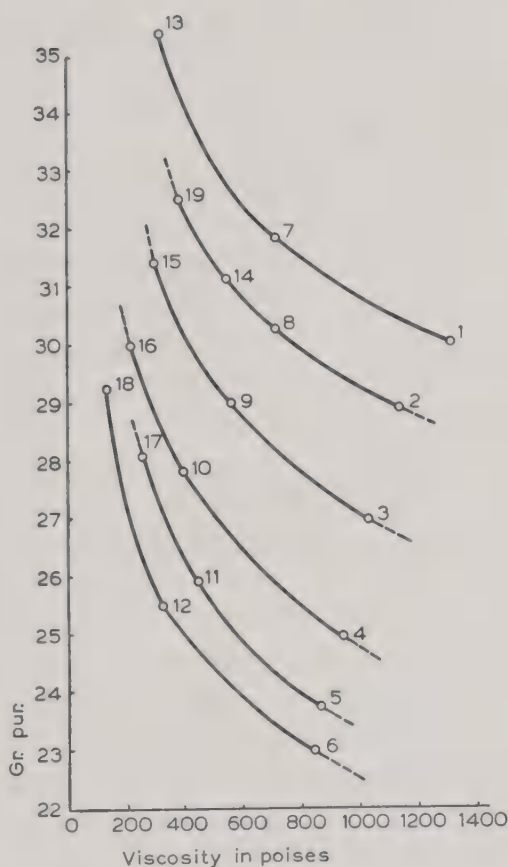


Fig. 14/10. Viscosity-purity relationship curves for mixtures of different hexose/ash ratio. (McCLeERY)

it is a suitable temperature for reheating a cooled massecuite, and 600 poises because modern plant should be able to work massecuites containing molasses of this viscosity.

Since the work of MICHELI and DE GYULAY has shown that minimum viscosities are often not far removed from those at 50° C no objection can

be made to the choice of this particular temperature on the grounds that selecting the theoretically more correct temperature of minimum viscosity would lead to a quite different target purity. It is further also clear that the method of finding a target purity as suggested by DOUWES DEKKER would be applicable only if the point of sudden increase of viscosity is well below 600 poises.

The target purity found by the Hawaiian method is representative of a family of molasses, on the other hand the composition of the nonsucrose is also representative and it is intelligible that attempts have been made to establish the association between this type of target purity and data characteristic for the nonsucrose composition. Most successful work in this field has been done by the staff of the Experiment Station of the Hawaiian Sugar Planters' Association, where the hexose/ash ratio was originally selected to typify nonsucrose⁵⁶. McCLEERY mixed samples of final molasses of two factories which differed widely in hexose/ash ratio's (*viz.* 0.74 and 3.21 respectively) in 6 different proportions and conducted boiling down (exhaustibility) tests on each mixture in an attempt to determine the purities and viscosities of those mixtures which were saturated at 50° C. The curves showing purities and corresponding viscosities for each mixture are shown in Fig. 14/10.

The collected data also enabled McCLEERY to construct curves showing the relationship between gravity purity and hexose/ash ratio for a number of viscosities. These curves are shown in Fig. 14/11.

From the curve for a viscosity of 600 poises the target purity of any molasses can be read, of which the hexose/ash ratio is known.

When, however, boiling down tests were carried out on molasses from factories other than the two which had provided the molasses which served for the construction of the curves, purities were found which were not always identical to the expected purities as read from the curve. This made it necessary to conduct from time to time boiling down tests on the final molasses of each factory and from the results of such tests a correction factor was calculated which had to be applied to the target purities as read from the standard curve (or a corresponding table) in order to obtain the so-called expected purity.

The mere fact that boiling down tests on certain molasses yielded target purities differing from those of the standard curve shows that identification of the nonsucrose of a final molasses by its hexose/ash ratio, although quite simple, is not accurate enough. Later on it was decided⁵⁷ that there was no real advantage in regularly conducting laborious boiling down tests on the final molasses of every Hawaiian factory. The corrections found in this

way were small (average for 1950: + 0.54), *i.e.* when compared with the weekly fluctuations normally occurring in the purities of final molasses they were not significant.

Weekly fluctuations of 'purities above expected' are normal and they

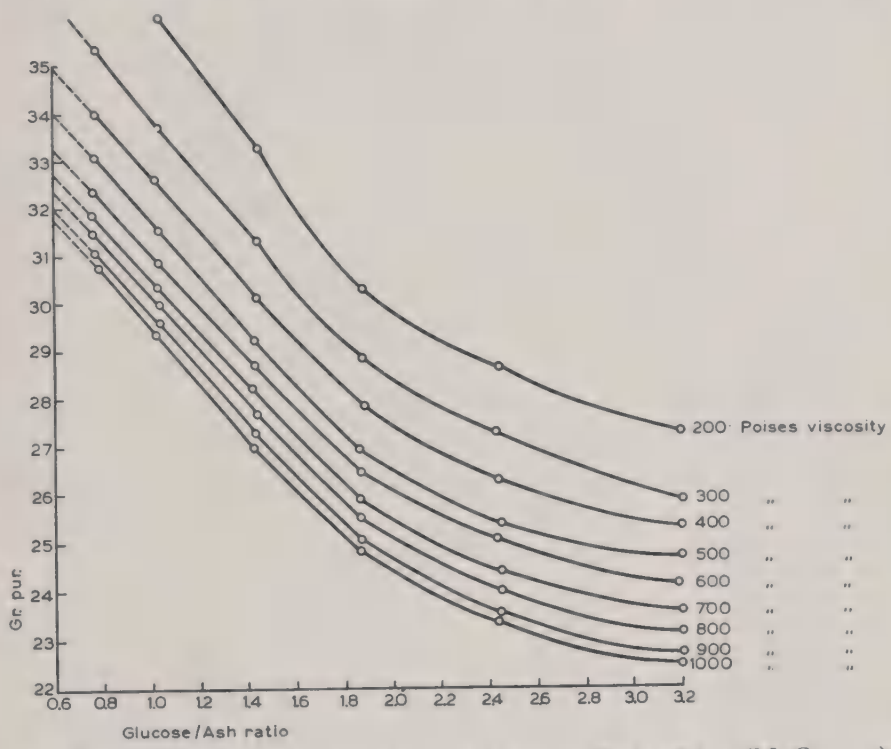


Fig. 14/11. Gravity purity and hexose/ash ratio relationships. (McCLeERY)

have significance only if they are over 2 points or show a definite trend from week to week.

Hence a new curve was constructed representing the relationships between refractometer/sucrose purity at 600 poises and the reducing substances/ash (carbonate) ratio of all molasses on which boiling down tests had been carried out between 1941 and 1950. The curve is a parabola of the formula

$$y = 42.15 - 9.0x + 1.35x^2$$

where

- y = refractometer/sucrose purity
- x = reducing substances/ash (carbonate) ratio.

In order to simplify the analytical procedure the use of the specific conductance instead of carbonated ash was also examined, and for a number of 1950 final molasses on which boiling down tests had been carried out it was found that the curve representing the average relationship between

refractometer/sucrose purity and reducing substances/specific conductance ratio fitted the various points even better. The formula for this curve (parabola) is

$$y = 38.55 - 61.9x + 49.9x^2$$

where

y = refractometer/sucrose purity

x = reducing substances/specific conductance ratio.

The specific conductance can be determined in a matter of minutes by simply diluting the sample to 28 refractometer brix and reading specific conductance on a conductivity meter.

According to the Official Methods of the Hawaiian Sugar Technologists for Control of Cane Sugar Factories, revised 1955, the Sugar Technology Department of the Experiment Station, H.S.P.A. has recently again modified the method of finding expected purities.

Two tables have been drawn up (Tables 3 and 4) relating the lowest attainable purity of any final molasses to either the reducing substances/ash (carbonate) ratio, or to the factor

$$\frac{\text{reducing substances \% refractometer solids}}{\text{specific conductance} \times 1000}$$

About the applicability of these tables to molasses of other countries, little information is available. HONIG⁴⁶ pointed out that the Hawaiian target purities are usually lower than those calculated using the formula given by DOUWES DEKKER⁴⁰.

Curves showing the viscosities of molasses of various purities at saturation and at certain degrees of supersaturation for a number of temperatures have also been determined by KELLY and McANTEE⁵⁸, who used a Technico viscometer, an instrument which according to ADKINS⁵⁰ is not very suitable for the purpose.

The authors – to set out graphically the relationship between viscosity, degree of supersaturation and temperature, for the construction of the diagram – successfully used a scale obtained from a paper by IRANY⁵⁹ which allowed a considerable reduction in the number of points required to draw a curve. IRANY namely had found that in a diagram in which the scale of viscosity is adjusted so as to make one ideal mixture appear as a straight line, all other ideal mixtures appear also as straight lines.

KELLY⁶⁰ divides families of final molasses into groups of good and bad viscosity characteristics and uses as criterion to decide into which group a final molasses falls, the steepness of the rise in the viscosity at decreasing

TABLE 3

EXPECTED PURITY OF FINAL MOLASSES FROM REDUCING SUBSTANCES-ASH (CARB.) RATIO
Refractometer sucrose purities at 600 poises and 50° C (122° F) saturation temperature.
Formula: RS/Ash (Carb.). (Official methods Hawaiian Sugar Technologists⁹)

Ratio	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
0.00	35.73	35.22	34.71	34.22	33.72	33.22	32.74	32.25	31.78	31.30	30.83	30.36
0.01	35.68	35.16	34.66	34.17	33.67	33.17	32.69	32.21	31.73	31.25	30.78	30.31
0.02	35.68	35.12	34.61	34.12	33.62	33.12	32.64	32.16	31.68	31.21	30.74	30.27
0.03	35.58	35.07	34.56	34.07	33.57	33.08	32.59	32.11	31.64	31.16	30.69	30.22
0.04	35.53	35.02	34.51	34.02	33.52	33.03	32.54	32.06	31.59	31.11	30.64	30.18
0.05	35.48	34.97	34.47	33.97	33.47	32.98	32.50	32.02	31.54	31.07	30.60	30.13
0.06	35.42	34.91	34.42	33.92	33.42	32.93	32.45	31.97	31.49	31.02	30.55	30.08
0.07	35.37	34.86	34.37	33.87	33.37	32.88	32.40	31.92	31.44	30.97	30.50	30.04
0.08	35.32	34.81	34.32	33.82	33.32	32.84	32.35	31.87	31.40	30.92	30.45	29.99
0.09	35.27	34.76	34.27	33.77	33.27	32.79	32.30	31.83	31.35	30.88	30.41	29.95
Ratio	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9
0.00	29.90	29.44	29.00	28.55	28.10	27.66	27.22	26.79	26.37	25.95	25.53	25.11
0.01	29.85	29.40	28.96	28.51	28.06	27.62	27.18	26.75	26.33	25.91	25.49	25.07
0.02	29.81	29.35	28.91	28.46	28.01	27.57	27.13	26.71	26.29	25.87	25.45	25.03
0.03	29.76	29.31	28.87	28.42	27.97	27.53	27.09	26.66	26.24	25.82	25.40	24.99
0.04	29.72	29.26	28.82	28.37	27.92	27.48	27.05	26.62	26.20	25.78	25.36	24.95
0.05	29.67	29.22	28.78	28.33	27.88	27.44	27.01	26.58	26.16	25.74	25.32	24.91
0.06	29.62	29.18	28.73	28.28	27.84	27.40	26.96	26.54	26.12	25.70	25.28	24.86
0.07	29.58	29.13	28.69	28.24	27.79	27.35	26.92	26.50	26.08	25.66	25.24	24.82
0.08	29.53	29.09	28.64	28.19	27.75	27.31	26.88	26.45	26.03	25.61	25.19	24.78
0.09	29.49	29.04	28.60	28.15	27.70	27.26	26.83	26.41	25.99	25.57	25.15	24.74

TABLE 4

EXPECTED PURITY OF FINAL MOLASSES FROM REDUCING SUBSTANCES-CONDUCTANCE RATIO
(Tentative)
Refractometer sucrose purities at 600 poises and 50° C (122° F) saturation temperature.

Formula: $\frac{RS \% \text{ Ref. Solids}^*}{Sp. \text{ Cond.} \times 1000}$. (Official Methods Hawaiian Sugar Technologists)

Ratio	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
0.00	35.42	34.68	33.97	33.27	32.60	31.95	31.33	30.73	30.15	29.60
0.01	35.35	34.61	33.90	33.20	32.54	31.89	31.27	30.67	30.10	29.54
0.02	35.27	34.54	33.83	33.14	32.47	31.83	31.21	30.61	30.04	29.49
0.03	35.20	34.47	33.76	33.07	32.41	31.77	31.15	30.55	29.98	29.44
0.04	35.13	34.39	33.69	33.00	32.34	31.70	31.09	30.50	29.93	29.38
0.05	35.05	34.32	33.62	32.94	32.28	31.64	31.03	30.44	29.87	29.33
0.06	34.98	34.25	33.55	32.87	32.21	31.58	30.97	30.38	29.82	29.28
0.07	34.90	34.18	33.48	32.80	32.15	31.52	30.91	30.32	29.76	29.22
0.08	34.83	34.11	33.41	32.73	32.08	31.45	30.85	30.27	29.71	29.17
0.09	34.76	34.04	33.34	32.67	32.02	31.39	30.79	30.21	29.65	29.12
Ratio	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5
0.00	29.07	28.56	28.07	27.61	27.17	26.76	26.37	26.00	25.64	25.32
0.01	29.01	28.51	28.03	27.57	27.13	26.72	26.33	25.96	25.61	25.29
0.02	28.96	28.46	27.98	27.52	27.09	26.68	26.29	25.93	25.58	25.26
0.03	28.91	28.41	27.93	27.48	27.05	26.64	26.26	25.89	25.54	25.23
0.04	28.86	28.36	27.89	27.44	27.01	26.60	26.22	25.86	25.51	25.20
0.05	28.81	28.32	27.84	27.39	26.97	26.56	26.18	25.83	25.48	25.17
0.06	28.76	28.27	27.80	27.35	26.92	26.52	26.15	25.79	25.45	25.14
0.07	28.71	28.22	27.75	27.30	26.88	26.48	26.11	25.76	25.41	25.11
0.08	28.66	28.17	27.70	27.26	26.84	26.44	26.07	25.72	25.38	25.08
0.09	28.61	28.12	27.66	27.22	26.80	26.41	26.03	25.69	25.35	25.05

* For the L & N Sugar Ash Bridge, or other instruments reading in micromhos, the equation becomes $\frac{RS \% \text{ Ref. Solids}}{\text{Bridge Reading} \times 1000}$

purity. A sample with a good viscosity characteristic is one in which the viscosity shows only a gradual rise with fall of purity for a particular saturation temperature. He experienced all stages between these and the steep rise associated with samples designated as having bad viscosity characteristics. He found that the viscosity at a saturation temperature of 55° C was associated with the true purity of the sample according to the general formula

$$\log y = \frac{10^k}{pm}$$

where

y = viscosity in poises
 P = true purity
 k and m = constants.

A good characteristic is for example given by the values 3.03 and 1.71 for k and m respectively, whilst a molasses of a bad viscosity characteristic under similar saturation conditions was found to have values of 5.79 and 3.31 for k and m respectively.

(d) *Progress in Molasses Exhaustion*

To what extent has the increasing knowledge of the principles underlying the crystallisation of sucrose from media of low purity improved the exhaustion of final molasses in cane sugar factories?

Early records of the composition of final molasses as discharged by Java factories enable us to reply to this question by comparing the actual purities with the target purities calculated with the formula given by DOUWES DEKKER⁶¹. Table 5 shows the relative data over a period of almost fifty years.

The data for 1892 are averages from analytical data published by PRINSEN GEERLIGS¹. Those for 1900 have been taken from a publication by PRINSEN GEERLIGS and ROSE⁶². Unfortunately they are not complete, and certain assumptions had to be made to calculate the target purity. The 1905 data have also been taken from a publication by PRINSEN GEERLIGS. They are the averages for 22 final molasses, 4 as discharged by carbonatation and 18 by defecation factories. The data for 1915–1941 are the means published in the *Java Annual Summaries of Factory Reports*. To calculate the difference between the true and the target purity the dry matter percentages were calculated according to SIJLMANS³⁶.

The overall improvement in the exhaustion between 1892 and 1941, taking into account the composition of the nonsucrose, has been just over

10 points. The unsatisfactory state of exhaustion in 1892 was to a large extent due to a high water content. In 1905 the water content was reduced by 6% to 18.3% and the mean difference above the target purity to 5.7. There are, however, reasons to suspect a high degree of supersaturation in the 1905 final molasses.

TABLE 5

EXHAUSTION OF JAVA FINAL MOLASSES IN A PERIOD OF HALF A CENTURY

Year	Dry matter %	True purity	Sulphated ash %	Red. sugars %	Difference above target purity
1892	75.7	46.6	7.47	22.0	10.1
1900	—	—	8.7	18.0	6-7
1905	81.7	42.8	9.35	23.5	5.7
1915	91.4 ¹	36.3 ²	8.9	29.3	3.3
1916	91.6	36.3	9.8	26.9	2.8
1917	91.2	36.5	8.8	27.6	3.3
1918	91.6	36.9	9.4	26.6	3.5
1919	92.3	36.2	9.7	27.7	2.8
1920	92.5	36.0	9.8	26.9	2.7
1921	92.5	36.2	9.7	27.3	2.4
1922	92.3	35.7	9.7	27.4	2.2
1923	92.8	34.9	10.2	26.7	1.2
1924	94.0	33.8	10.5	27.5	0.1
1925	92.6	34.6	10.2	28.3	1.0
1926	92.6	34.0	10.5	29.4	0.6
1927	92.8	33.6	10.8	28.1	-0.1
1928	93.1	34.4	11.3	26.8	0.4
1929	93.4	35.1	11.7	25.7	0.9
1930	93.6	35.1	12.3	25.1	0.7
1931	93.2	34.8	11.8	26.6	0.7
1932	93.4	34.9	12.3	25.7	0.6
1933	94.1	34.5	12.4	25.9	0.2
1934	93.7	34.6	11.7	26.9	0.6
1935	94.3	35.4	12.7	25.0	0.9
1936	94.3	35.8	13.8	23.3	0.8
1937	94.4	35.4	13.0	24.5	0.8
1938	94.9	34.8	13.3	24.4	0.1
1939	95.0	34.6	13.3	24.3	-0.2
1940	95.0	34.9	13.4	24.0	0.1
1941	95.1	35.0	13.6	23.4	0.1

¹ Spindle brix (1 + 9 dil.) in the years 1915-1941.

² Sucrose/brix purity in the years 1915-1941.

In the decade between 1905 and 1915 the average state of exhaustion was improved by another 2.5 points. From 1915 onwards annual data are available. They indicate that manufacturers succeeded in gradually increasing the brix of final molasses from approx. 91.5 to 95.0 in the period 1915-1941. This was accompanied by a reduction in the difference over the target purity of just over 3 points. The purity, however, was not reduced to the

same extent in this period due to the composition of the nonsucrose becoming gradually more unfavourable to good exhaustion, as is shown by the increase in the ash percentage and the drop in the reducing sugar percentage. This shows that a conclusion based merely on the annual mean purities – without taking into account alterations in the composition of the nonsucrose – would have resulted in an incorrect impression of the improvement made in the exhaustion of final molasses in this period.

The reason for the increase in the ash content of the Java molasses is not known, but may be connected to the increased use of fertilisers in the cane fields.

The continuous drop in the difference above the target purity in the years directly after 1918 deserves some attention. Here we very likely observe the effect of the investigations by VAN DER LINDEN. They had taught that longer and deeper cooling of the low grade massecuites, at a low water content of the liquid phase, must result in a lower purity.

The objection to the increased stiffness of the massecuite was neutralised by VAN DER LINDEN by his advice to add approx. 15% of diluted molasses (83–85° brix) to ‘lubricate’ the material instead of addition of water which might dissolve crystallised sucrose.

Another period of continuous improvement, although less striking, commences in 1935 and is probably associated with the interest shown by Java factories in the regular comparison of actual purities of final molasses with the target purities published by SIJLMANS in monthly and annual summaries.

The outbreak of the World War II interrupted efficient processing in Java and prevented a new feature in manufacturing technique from finding expression, *viz.* the introduction of high speed centrifugals.

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